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ABSTRACT

Critical properties required of an oxidation resistant coating on carbon, revealed by a literature review of existing coating methods, were used to identify SiC as the most cost-effective single coating material. Plasma arc spraying was used to produce several porous coatings on an electrode graphite, but it proved impossible to coat SiC satisfactorily. A SiC coating was developed from tetraethyl ortho silicate (TEOS) sol-gel using a phenolic resin as a carbon source by firing to 1450 °C. The oxidation resistance of the SiC coating on an electrode graphite at 920°C was improved if the rate of gelation/ageing of the sol was slower than the rate of drying. Using this principle, an optimised SiC coating was developed. Further improvements in oxidation resistance were sought by developing sol-gel derived multilayercoatings of SiC with a glassy overlayer. Based upon a literature survey, a SiO_2-TiO_2 glass and a SiO_2-Al_2O_3-LiO_2 glass-ceramic coating were selected and applied to a fine grained Poco graphite and a 2-D carbon-carbon composite (C/C) previously coated with SiC. For the SiO_2-TiO_2 glass a firing procedure was developed which inhibited the formation of undesirable TiC. The SiC/SiO_2-TiO_2 coating, after firing to 1600 °C, improved the oxidation resistance at 1200 °C of the C/C composite, but produced no additional benefit on Poco graphite, compared to the SiC coating. The SiC/SiO_2-Al_2O_3-LiO_2 coating slightly improved the oxidation resistance of the C/C composite, compared to the SiC/SiO_2-TiO_2 layer, and was also superior to the SiC/SiO_2-Al_2O_3-LiO_2 coating on Poco graphite.

INTRODUCTION

The development of new high temperature materials for more sophisticated industrial applications has been intensively pursued in recent years. High-temperature superalloys can be only used up to 1100°C, monolithic ceramics and ceramic matrix composites have been developed for use at temperatures up to 1300°C and 1650°C, respectively, but only carbon materials have potential to be used up to 2500°C (Miller - 1982). The preconditions, which are well met by conventional graphites and carbon-carbon composites, for a material to be called a high temperature one are: thermal stability as a solid, high resistance to thermal shock, due to high thermal conductivity and low thermal expansion behaviour, and high strength and stiffness in high temperature applications (Fitzer - 1987).

Carbon is a unique solid substance that can be made to exhibit a very wide variety of different structures and properties. Some carbons are extremely strong, hard and stiff, while other forms are soft and ductile; some of them are highly porous and exhibit a large surface area, while others are impervious to liquids and gases (Fitzer - 1987). The properties and qualities cited above allied with the high degree of chemical inertness are promoting the substitution of traditional materials by different types of carbons. However, in spite of their versatility and potential, all carbons exhibit a major disadvantage that is rapid oxidation at temperatures as low as 500°C.

Several studies have been made on the effect of the oxidation of carbon materials on their thermal and mechanical properties. Rabotnov (Rabotnov - 1978) studying the effect of oxidation on the mechanical properties of carbon-carbon composites, concluded that without protection this material could be only used at temperatures below 450°C, a drastic limitation for a material with potential to operate up to 2500°C. Zhao (Zhao - 1981) showed that for a total burnoff of about 20% the Young's moduli and the shear moduli of commercial polycrystalline graphites were reduced to 30% of the original value. Ragan (Ragan - 1983) concluded that a small burnoff (around 1%) significantly reduced the strength of needle-cokes, as was also found with graphites (Zhao - 1981). Thrower (Thrower - 1982) verified that 9% weight loss, due to the oxidation of the isotropic graphite H-440, caused a 50% strength loss. Pickup (Pickup - 1986) measured the critical stress intensity factor, dynamic elastic modulus and three-point bend strength of two different nuclear graphites, before and after oxidation, and observed a reduction of between 40% and 50% in each of the properties for 7% weight loss. The results presented by Zhao (Zhao - 1985) showed that oxidation had a catastrophic effect on the mechanical properties of carbon-carbon composites and oxidation to 20% burnoff resulted in a 75% reduction in Young's modulus and 64% reduction in the flexural strength. Crocker (Crocker - 1990) found that 10% burnoff caused 26% reduction in dynamic modulus and 48% reduction in flexural strength for carbon-carbon composites.

Because of this limitation a considerable amount of work has been devoted to the development of methods to improve the oxidation resistance of carbon. Although some success has been achieved, there are still many potential applications of carbons where performance is limited by poor oxidation resistance, particularly at temperatures above 1200°C. Developments in coatings and other techniques offer potential for improving oxidation resistance of carbons still further and for reducing the present cost of this benefit. It is for these reasons that the work related in this thesis was undertaken.

The overall aims of this work are to explore new methods for producing coatings to inhibit oxidation of carbon materials which are capable of modification for different high temperature applications. The plasma arc spray method was initially investigated because the literature survey presented in Chapter I did not dismiss this technique that have been industrially used to inhibit the oxidation of electrode graphites. The study of the plasma arc spray method is presented in Chapter II but the bulk of the work presented in this thesis is devoted to the development of coatings prepared by sol-gel methods, since this approach has received very little attention in the past. Background to the method, the criteria for the choice of layers in the multilayer system adopted and the selection of the composition of the gels with their preparation are presented in Chapter III. Chapter IV presents the results achieved with the sol-gel technique while Chapter V is dedicated to their discussion. Conclusions and suggestions for future works are summarized in Chapter VI.

CHAPTER I

MODIFICATIONS OF CARBON MATERIALS TO INHIBIT OXIDATION - THE STATE OF THE ART

I.1 - INTRODUCTION

In 1934, a method for inhibiting the oxidation of graphite was patented, for the first time, by Johnson (Johnson - 1934). This method consisted of a coating system composed of an inner SiC layer and an outer glaze of B_2O_3. The beneficial properties of silicon carbide combined with glassy materials in inhibiting the oxidation of graphite have been recognized since that time.

The main obstacle to apply an external protective barrier on the carbon surface is undoubtedly the low coefficient of thermal expansion (CTE) of carbon materials, and especially carbon-carbon (C/C) composites, in comparison with the CTE of potential refractory inhibitors. This was realised by Johnson (Johnson-1934), since part of the function of the B_2O_3 was to fill cracks in the SiC layer formed as a result of internal mismatch with the graphite substrate. Nowadays the development of advanced C/C composites, with lower CTE, and operating at very high temperatures in aerospace environments require more efficient ways of inhibiting the oxidation of carbon materials.

Different methods, processes and materials have been develloped for this purpose and their inter-relationship does not make it easy to arrange them in a simple and straightforward way. For a systematic review, the work will be divided between internal and external protection methods. The external protection methods will include any technique that results in a coating on the carbon surface; all the others will be classified as internal protection methods.

I.2 - REVIEW OF THE LITERATURE

I.2.1 - INTERNAL PROTECTION METHODS

The most common methods used to modify, internally, carbon articles to improve their oxidation resistance are: (i)direct removal and/or deactivation of catalytic impurities, (ii)incorporation of oxidation inhibitors, (iii)total or partial substitution of the carbon-carbon composites matrix material by a more oxidation resistant one.

i) DIRECT REMOVAL AND/OR DEACTIVATION OF CATALYTIC IMPURITIES

Since 1942 chlorine and fluorine gaseous compounds have been used extensively during the graphitization step to remove impurities from nuclear graphites. The improvement in the oxidation resistance of graphites by removal of catalytic impurities with chlorine compounds was studied by Baker (Baker - 1983) and McKee (McKee - 1985). Baker verified that CCl_4 vapour was able to poison a platinum catalyst during graphite gasification while McKee (McKee - 1985) measured the reduction of the oxidation rate of graphite, at temperatures higher

than 800°C, when it was treated with gaseous CCl_4, $CHCl_3$ and C_2HCl_3. Other acid treatments have been tried with the same objective and Hippo (Hippo - 1987) observed some positive results with phosphoric acid and even acetic acid.

ii) THE INCORPORATION OF OXIDATION INHIBITORS

ii.a) in graphite bodies, pitches and resins

The development of JTA graphite-based refractory composites, developed by the Union Carbide Co.(Union Carbide - 1964), is possibly the best example of the inhibition of the oxidation of graphite bodies by the addition of inhibitors. The composites consist of mixtures made up primarily of graphite and zirconium and zirconium diboride or zirconium carbide with small additions of silicon and columbium. X-ray analysis of the unoxidized material showed the presence of zirconium diboride, silicon carbide and graphite, but after exposure at 2475 K, in a dynamic airstream, only the presence of the oxide of zirconium and zirconium silicate were identified (Buckley - 1967). The following reactions were proposed to explain the coating mechanism (Buckley - 1967).

$2C + O_2 \text{ ---> } 2CO(g)$ (1)

$C + O_2 \text{ ---> } CO_2(g)$ (2)

$2SiC + 3O_2 \text{ ---> } 2SiO_2(l) + 2CO(g)$ (3)

$2ZrB_2 + 5O_2 \text{ ---> } 2ZrO_2(s) + 2B_2O_3(l)$ (4)

$ZrO_2 + SiO_2 \text{ ---> } ZrSiO_4$ (5)

It seems that this was the first time a chain-like system was planned to provide oxidation protection in a sequential range of temperatures and with different compounds, i.e: molten boron oxide (equation 4) was formed to protect graphite from 723 K (melting point) up to approximately 1530 K (vaporization temperature), silica (equation 3) was formed to protect graphite up to 1905 K when it starts to be reduced by carbon and vaporizes as silicon monoxide. Zirconium silicate (equation 5) should protect graphite up to 1760 K when it starts to decompose and, finally, molten zirconium oxide (equation 4) should protect graphite up to the final operating temperature, 2975K (Buckley - 1967).

The mixture of graphite with zirconium diboride and silicon was investigated in more detail by several other researchers in order to explain the reduction of weight loss in air of around two orders of magnitude, when this material was compared with VPP grade graphite (Zelikson - 1973, Krivoshein - 1978). The oxidation resistance of such composites was attributed to the formation of a surface borosilicate oxide film containing boric anhydride, silica and zirconia. However it became prone to crack during thermal shocks and, apparently, no longer formed a continuous surface layer when the boric anhydride vaporized and the film became enriched in the refractory components ZrO_2 and SiO_2 (Zelikson - 1973). The addition of vanadium and niobium, to the mixture described previously, improved the oxidation resistance at temperatures between 1200-1800^{o}C, under natural air circulation conditions for 15 min; vanadium was more effective than niobioum (Krivoshein - 1978). It was verified that the oxidation of the system (ZrB_2-SiC-C-V) resulted in the formation of a complex oxide

film consisting of a mixture of oxides V_2O_3, V_2O_5 and B_2O_3 (Samsonov - 1975).

The results obtained in the works cited above lead to further investigations of boron and zirconium compounds which were able to form an oxide film by in situ oxidation. Miyazaki (Miyazaki - 1981) made graphite and boron carbide composites, by hot-pressing, and verified that with a small amount of B_4C, the composites showed higher oxidation resistance than conventional graphites while McKee (McKee - 1981) observed the inhibition of the oxidation of graphite with addition of boric acid and its derivatives.

A comparative study of the oxidation rate of Zr-ZrC-C and Ti-TiC-C composites (Kostikov - 1981), at 1170-1770K, showed that the titaniumized graphite exhibited higher oxidation resistance than the zirconized graphite and, therefore, the real protective effect of zirconium oxide should be reviewed.

A different research line lead to some experimental investigations of the properties of phosphorus compounds, not only when they were added to the carbon body, but also to the raw materials during the manufacturing process. It was recognized that phosphates could deactivate catalytic impurities in the carbon by converting them to stable phosphates which could not participate in oxidation-reduction cycles (McKee - 1981). Phosphorus oxychloride was recognised as the most powerful inhibitor known for the graphite

oxidation reaction (McKee - 1981). Recently carbonized cokes, produced from Ashland A240 petroleum pitch and Allied 15V coal tar pitch with additions (3% by weight) of silicon chloride, phosphorous V chloride, surfuryl chloride and chloroform, were used to evaluate the effect of such chemical compounds on the coke's oxidation rate (Murdie - 1988). The results showed that phosphorous V chloride and surfuryl chloride decreased, while silicon chloride increased, the rate of burnoff (Murdie - 1988).

ii.b) in fibers

The idea of improving the oxidation resistance of carbon fibers started in the early stages of the development of C/C composites and the kind of chemical compounds used did not differ very much from those already cited for graphite protection, i.e., boron and phosphorus compounds. Ehrenreich (Ehrenreich - 1978) dispersed several refractory metal borides, such as titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten, as well as boron containing additives (boron nitride, boron silicide or elemental boron) between the fiber layers, as the fibrous shape was being produced. An improvement of the oxidation resistance was achieved and the same author observed that protection of the carbon material with boron nitride or boron silicide was preferred.

Although the inhibiting effect of boron compounds on the oxidation reaction was well known in 1987, very few studies were

dedicated to explain the mechanism. It was known that boron could enhance the graphitization process, reducing defects in the micro-structure and, therefore, improving the oxidation resistance of carbon materials. It was generally accepted that boron compounds left a protective boron oxide coating that acted as a barrier to oxygen diffusion and that with 2%wt of B_2O_3 it would be possible to form a continuous film on the carbon surface (Ehrburger - 1986). It was also known that at lower concentration there was a tendency for B_2O_3 to segregate in clusters on active sites and so inhibit the oxidation reaction (McKee[2] - 1984, Ehrburger - 1986). However, Jones (Jones - 1987) showed that boron doped pitch fibers exhibited higher resistance to oxidation even at B concentrations of 40 ppm. The boron did not influence fiber graphitization or did it form a boron oxide layer. The enhanced oxidation resistance was attributed to the presence of substitutional B and was most noticeable when the B concentration in the fiber was very low (Jones - 1987).

The most comprehensive invention to inhibit the oxidation of carbon fibers (Saito - 1980), in particular acrylic-based carbon fibers, included incorporation of phosphorus, boron, zinc and calcium compounds into the polymer melt prior to spinning the acrylic fiber precursor. The compounds were also deposited on the fiber surfaces, in a single or multiple steps, by impregnation or spraying with an aqueous or organic dispersion. Although an improvement in the oxidation resistance was claimed in several examples, even for calcium compounds (Saito - 1980), Smith (Smith - 1968) had earlier connected

the high oxidation resistance of carbon fibers to low alkali content and Seegel (Seegel - 1981) showed that, in particular, sodium impurities lead to large local craters on the surface of PAN-based carbon fibers.

ii.c) in C/C composites

In most of the studies in this area the inhibitors, in powder form, were added to the impregnating resin or were embedded in the impregnated preforms.

The most important results were presented by McKee (McKee - 1988) who investigated the oxidation behaviour of matrix-inhibited C/C composites and uninhibited C/C sheet materials. The substrates were densified with a four-cycle impregnation/pyrolysis process with furfural-resorcinol resin or a blend of coal tar pitch and phenolic resin or coal tar pitch alone. Some composite materials contained zirconium boride and submicron boron particles that had been added to the prepeg resin and others contained fine particles of boron carbide, silicon carbide and zirconium boride also added to the prepreg resin before carbonization. It was verified that in neither case was the distribution of additive uniform throughout the composite, but the weight losses at a given temperature were markedly lower for the samples with additives than for the unmodified C/C composites (McKee - 1988). A dependence of reactivity on exposure time, at temperature (between 500-1000^{o}C), was observed and assumed to be due to the slow dispersal of inhibiting material throughout the composite pore

space and the effect was particularly well-marked for the materials that contained particulate boron and zirconium boride (McKee - 1988).

A mixture of chromium powder and alumina powder activated with NH_4Cl, was used by Han (Han - 1987) to develop a high temperature antioxidation treatment for C/C composites. The preforms of the C/C composites were made of a stack of two-dimensional carbon fabrics woven from polyacrylonitrile fibers. The preforms were preimpregnated by resin; densified by repeating the impregnation of pitch or pitch and/or SiC and baking. The mixture of chromium powder, alumina powder and/or a small quantity of the activator of NH_4Cl was added and the system finally reacted at 1000^oC, under argon atmosphere for several hours. Han (Han - 1987) measured the oxidation rates for the C/C and the C/C/SiC composites and verified that: a) the C/C composites were more reactive, at 600^oC, than the C/C/SiC composites but above this temperature the addition of SiC had no effect on the retardation of oxidation of the material; b) the chromium coating formed by the solid-state reaction, between the chromium powder and the C/C composite, decreased the oxidation rate up to 900^oC; c) it was difficult to make the C/C composites and chromia compatible because of the different bonding characteristics of these two materials and it was recommended to apply a chromium carbide layer between the C/C composite and chromia for improving the compatibility between these materials (see McKee[1] - 1986 in item I.2.3 - Comparative Studies).

iii) TOTAL /PARTIAL SUBSTITUTION OF THE CARBON-CARBON COMPOSITE MATRIX

The partial substitution of the C/C matrix composite by a more oxidation resistant material is possibly the most common technique in use nowadays to provide an internal protection to C/C composites. Silicon carbide was the first material infiltrated (Christin - 1980, Naslain - 1980) and, after several trials, a mixture of methyltrichlorosilane and hydrogen was selected as the infiltrating gas. The two main limitations to successful infiltration were found to be the closing of internal porosity by the "bottle-neck" phenomenon and faster deposition in pores near the surface than inside the core (Christin - 1980, Naslain - 1980). The same authors determined that it was essential to work at as low temperature as possible to limit the speed of reaction at the surface. It as also advisable to reduce the gas pressure, in order to increase the mean free path of the gas molecules and promote diffusion into the interior of the pores. These authors claimed that a replacement of only 20% by volume of the carbon matrix by SiC reduced the weight loss in air, at 1500°C, by a factor of 12 while the compressive strenght, interlaminar shear strength and modulus of elasticity increased by a factor from 2 to 4.5 times. The same technique was tried with titanium carbide (Naslain - 1981, Rossignol - 1982) which has a higher thermal stability than SiC and good chemical compatibility with carbon at high temperatures. The comparative results indicated that in the case of the C/TiC matrix air-oxidation of the composites became significant during a 7-hour test above 800-900°C. For the C/SiC matrix oxidation of the composite only became significant above 1500-1600°C (Naslain - 1981). These results indicate that a TiO_2 film formed from TiC is not as effective as a SiO_2 formed

from SiC in protection C/C composites from oxidation (Rossignol - 1982).

The successful infiltration of SiC to substitute partially the carbon matrix in C/C composites, allied with the well known inhibitor effect of boron compounds on the oxidation reaction, lead Hannache (Hannache - 1984) to infiltrate boron nitride in a porous 2D-carbon-carbon preform. It was verified that BN deposition occurred within the pores rather than on the external surface of the samples, leading to a progressive in depth densification of the initial 2D-C-C porous preform. Comparative tests showed, however that the oxidation resistance of 2D-C-C/BN composites was lower than that of the related 2D-C-C-/SiC composites due to the higher thermal stability and lower volatility of SiO_2 compared to B_2O_3 (Hannache - 1984).

Instead of infiltrating a porous carbon matrix, Jawed (Jawed - 1986) decided to react carbide-forming organometallics with the resin to develop a modified carbon matrix. A polycarbosilane was used as the precursor of silicon carbide, but X-ray diffraction did not detect the presence of SiC or SiO_2 in all the samples after carbonization. Only after oxidation at 1500°C was SiO_2 detected in all of the samples and it was determined that below 1000°C, SiC did not oxidize to SiO_2 and therefore can not protect carbon from oxidation below this temperature (Jawed - 1986). Diphenylborosiloxane was also used, as the precursor of B_2O_3 and SiO_2, however its addition did not improve the oxidation

resistance of the carbon systems as much as the polycarbosilane (Jawed - 1986).

I.2.2 - EXTERNAL PROTECTION METHODS

The main problem observed in all the external protection methods is related to the very low CTE exhibited by carbons materials ($-1.5x10^{-6}/^{o}C$ - Advanced C/C composites, $7x10^{-6}/^{o}C$ - Poco Graphite ZXF 5Q) when compared with the potential protective coatings (Criscione-1964, Macklin-1967, Rabotnov-1978, Curry-1979, Smialek-1985, Rumler-1983, Holzl-1985, Okamoto-1986, Jawed-1986, Copley-1987, McKee-1987, Stinton-1988, Buckley-1988, Strife-1988, Huetner-1988). As the CTE of the coating does not match the CTE of the substrate, microcracks are developed in the refractory layer when the coating is applied and/or during heating cycles, promoting a catastrophic oxidation of the carbon substrate. A theoretical analysis of the oxidation of carbon-carbon composites (Luthra - 1988) showed that even a 10 nm wide crack could provide paths for rapid diffusion of oxygen.

To classify studies published in this area proved more difficult than was the case for internal protection methods, due to a greater variety of materials and techniques used. Among the several options it was preferred to classify the research work by the coating method

employed. Therefore, this section is divided into: i) impregnation methods; ii) spray methods, including flame spray, air spray and plasma arc spray; chemical vapor deposition (CVD); iii) the conversion process (the Silmor process); iv) pack process; v) and other methods and/or techniques.

i) THE IMPREGNATION PROTECTION METHOD

The impregnation method appeared as the most obious technique available to cover the external surface of carbons and their surface porosity, since it is a well known step in the manufacture of graphite and C/C composites to increase their density.

The most common chemical compounds used to impregnate carbon materials were, again, boron and phosphorus compounds whose inhibitor properties were demonstrated when the internal protection methods were described.

One of the major problems using boron compounds is their hygroscopicity and it was once reported (Thomas - 1965) that boron oxide deposited on graphite inhibited the gasification of the carbon in dry oxygen, at temperatures around 800°C, but acted as a catalyst in moist oxygen. These results were not confirmed by Allardice (Allardice - 1970) and Woodley (Woodley - 1968,1969) who showed that graphite doped with boron exhibited lower oxidation rates both in dry and moist

oxygen. McKee (McKee[2] - 1984) investigated the effect of boron compounds on the oxidation rate of pure graphite powder by vacuum impregnating the samples with boric oxide, ammonium borate, benzene boronic acid, trimethylamine borane, trimethyl borate, triethyl borate, tri-tert-butyl borate and triamyl borate. It was verified (McKee[2] - 1984) that the presence of as little as 2 wt.% B_2O_3 reduced the oxidation rate of graphite by a factor of about five at 800°C and that liquid organoboron compounds, such as the alkyl borates, were more effective oxidation inhibitors than B_2O_3 applied from solution. It was also shown (McKee[2] - 1984) that in the presence of water vapour, the oxidation rate of pure graphite was somewhat retarded compared with that in dry air. The borate doped sample, however, oxidized at a slightly greater rate in the presence of water vapour but, even so, the average oxidation rate was still reduced by a factor of about 5 when compared with the unprotected graphite. The hygroscopic effect of boron oxide was also observed when C/C composite samples were vacuum impregnated with liquid tri-tert-butyl borate, dried and hydrolyzed in air and covered with powdered boric acid, boron oxide or ammonium borate (McKee[2] - 1986). Figure 1 shows that this treatment protected the carbonaceous substrate from oxidation, in air, for extended periods at temperatures up to 1000°C but it was concluded, again, that the coatings were less effective in the presence of water vapor. Neri (Neri - 1980) used a water solution with 8% of ammonium pentaborate to impregnate electrolysis anodes. A weight loss of 20 % on the treated samples, at 550°C, instead of 87 % on the original material was measured in oxyreactivity tests (Neri - 1980).

The boron oxide film that is left to protect carbon surfaces against oxidation reaction volatilizes at relatively low temperatures and this constitutes an additional problem when the carbon material is to be used at temperatures above 1100-1200°C. Several workers studied the addition of Na_2O to modify the composition of the boron-glass film, formed on the graphite surface, in order to increase the operating temperature of this glassy coating (Litvinov - 1968, Appen - 1953, 1974, Mazalev - 1958, Mazurin - 1985, Samsonov - 1960, Gol'dshtein - 1980). The last work showed that the thermal stability of glasses in the H_3BO_3-NaB_4O_7 system successively decreased on going from boric acid to borax and that the oxidation of the substrate increased with the addition of Na_2O.

The protective effect of phosphorus compounds impregnated into carbon materials are very well illustrated in the work of McKee (McKee[1] - 1984) and Kindler (Kindler - 1983,1985). A large number of phosphates and phosphite esters were vacuum impregnated into graphite samples and heat-treated (McKee[1] - 1984). A significant increase in the oxidation resistance in air, up to 1000°C, was observed for the treated samples (Figure 2) and the effectiveness of the various adsorbates, as oxidation inhibitors, were found to be dependent, not only on the chemical nature of the organo-phosphorus compound, but also on the heat treatment procedure with phosphates being more effective in promoting water adsorption than phosphites (McKee[1] - 1984).

Other attempts that have been made to inhibit the oxidation of carbons through the impregnation method are: a) the impregnation of C/C composites by polyfurfuryl alcohols, phenolic resins, and pitches (Williams - 1975) particularly when silicon compounds were added in attempt to form SiC on pyrolysis, b) the use of H_3PO_4, ZnO, $Al(OH)_3$, $CuSO_4$ and $Cu(NO_3)_2$ (Baranski - 1982) to impregnate graphite electrodes, c) the impregnation of pure graphite powder with CCl_4, $CHCl_3$, C_2HCl_3, adypoyl chloride, hexachloracetone and hydrochloric acid (McKee - 1985). The results showed that: a) when silicon-phenolic resin was used, the oxidation resistance of the C/C composite samples was improved (Williams - 1975), b) impregnation with inorganic salts improved the resistance to oxidation, but oxidation inside pores dominated in the case of the impregnated material, whereas external and internal oxidation were comparable for unimpregnated graphites (Baranski - 1982), c) CCl_4, $CHCl_3$ or C_2HCl_3 had little effect on the oxidation behavior, however the impregnation of graphite with adypoyl chloride, hexachloracetone and hydrochloric acid reduced strongly the oxidation rate (McKee - 1985).

ii) THE SPRAY METHOD

Plasma arc-spray is certainly a technique with high potential when high temperature protection of carbons is desired. In several cases, additional treatment was done to reduce the porosity and amount of gases trapped into the coating and to enhance its adhesion

to the substrate. Some studies were designed to improve the application technique rather than the inhibition of the oxidation (Konokotin - 1983, Kostikov - 1978, Alekseev - 1984, Elyutin - 1969). Konokotin (Konokotin - 1983) applied a coating consisting of mixtures of aluminium and alumina, over graphite, and found that the minimum layer porosity was detained at a spraying distance of 150-190 mm, for all the mixtures. The maximum strength of the bond, between the coating and the substrate, was detained at a spraying distance of 150 mm, for aluminium containing 70% alumina (Figure 3), for all the temperatures. Based on the work presented by Kostikov (Kostikov - 1978), Alekseev (Alekseev - 1984) developed a thermal fatigue resistance test for rapid evaluation of heat-shielding coatings applied to graphite. The effect of protective atmosphere and substrate temperature on the properties of molybdenum coatings on graphite were investigated by Elyutin (Elyutin - 1969) . A vacuum chamber, preevacuated to $1x10^{-6}$ mm Hg and filled with grade A argon, was used to eliminate the shortcomings of plasma-sprayed molybdenum coatings. The substrate temperature was varied within 20-1500^{o}C and it was observed that the bond strength was affected by oxygen which aids chemical bond formation at lower temperatures while, in argon, the coating began to bond to graphite when the temperature of the substrate approached 800^{o}C and the strongest bond was formed at 1200^{o}C.

The most extensive work, using the plasma-arc spray technique, aiming to protect carbons at high temperatures was presented by Wright (Wright - 1968) based on the promising properties exhibited by iridium (Criscione - 1964), e.g., low permeability to oxygen diffusion at

1980°C, no reaction with graphite below 2290°C, very low vapor pressure and low oxidation rate. Wright (Wright - 1968) studied the fabrication of iridium and iridium-alloy coatings, on graphite, by plasma-arc deposition, followed by gas-pressure bonding. Wright tried to avoid several drawbacks such as continuous porosity, cladding defects and lack of uniformity, normally found when slurry dip, vapor plating, foil cladding and electroplating were used. The gas-pressure bonding technique was used to achieve full density in the coating and to extrude iridium into the open porosity in the graphite. In this method the as-plasma-coated parts are encapsulated in metal containers, sealed by electron-beam welding, and then subjected to high-pressure and high-temperature in a cold-wall autoclave. Close examination of the iridium-graphite interface in the specimens, after the gas-pressure bonding treatment, revealed the presence of a reaction layer (Wright - 1968). It was postulated that oxygen in the coating, either as a result of the coating process, or from the substrate, reacted with the iridium to form an oxide that reacted with diffused carbon or hydrocarbon, producing vapour-deposited iridium at the graphite interface (Wright - 1968). When the substrate was outgassed at 1370°C, to eliminate oxygen, followed by a second outgassing at 1200°C, after that iridium was sprayed, to eliminate the iridium oxide, the amount of porosity and the swelling effect of the coating observed during the heat treatment, at 2000°C, was greatly reduced. Although application of this set of techniques has not so far resulted in successful inhibition of the oxidation of carbons, the use of iridium allied to an easy and economical way of applying it, is still open for further investigations (Strife - 1988).

The work of Burykina (Burykina - 1965) is possibly the most comprehensive one using plasma arc spray although the effectiveness of plasma arc sprayed coatings in increasing the oxidation resistance of carbons was not investigated. The possibility of obtaining coatings of copper, aluminum, nichrome, molybdenum and tungsten, on graphite, by plasma deposition, and coatings of titanium, zirconium, niobium and silicon carbide by applying a metallic layer with subsequent diffusion treatment was investigated. The main parameters of the technique were optimized in each case and when a metallic layer was applied (copper, aluminum, nichrome, molybdenum and tungsten) it was heated in a vacuum resistance furnace, to a temperature of 50-100°C above the melting point of the metal to permit the metal to melt and flow over the surface of the graphite specimen and cover it with a uniform layer (Burykina - 1965). The titanium, zirconium, niobium and silicon coatings were converted into carbides by heat treatment at specific time and temperatures (Burykina - 1965): Ti - 2 hours at 1500°C, Zr - 2 hours at 1800°C, Nb - 2 hours at 1900°C, Si - 1.5 hours at 1600°C and 1.5 hours at 2200°C (at which temperature the allotropic transformation of ß-SiC to α-SiC occurred).

Low temperature oxidation resistant coatings (1000°C), mainly on electrode graphite, have been systematically applied in industry using the air spray technique. There are two main routes in this area, i.e., the spray of multilayer coatings using a slurry of metallic powders in nitrocellulose lacquer or glassy coatings produced via a sol-gel technique. When a slurry of metallic powder is applied it may be preceded by spraing a metallic bond coating, usually aluminium, that is melted on the graphite surface using a graphite electrode arc.

Application of this set of coatings, i.e., the metallic bond coating and the slurry of metallic powder, is repeated several times up to 1mm thickness. Smialek (Smialek - 1983,1985) claimed the development of a new oxidation resistant coating, produced by applying a slurry of Ni-Si and Al-Si powders in a nitrocellulose lacquer. These powders were vacuum sintered and cyclic oxidized from room temperature up to 1200°C and it was observed that while the Al-Si coatings evaporated extensively during sintering, providing incomplete coverage and poor oxidation protection, the Ni-Si coatings did not evaporate and could be processed to provide a uniform outer layer of Si, SiC and Ni-Si compounds. The author (Smialek - 1983,1985) concluded that this study elucidated the behavior of various Ni-Si slurry coatings, but it did not lead to a workable oxidation-resistant coating. Polyphosphate glasses produced from gels and coacervates were used by Vast (Vast - 1988) to inhibit the oxidation of electrode graphites. Two ternary gels, P_2O_5-Na_2O-Al_2O_3 and P_2O_5-Na_2O-MnO were selected, and Cr_2O_3 was used as a ceramic powder additive. Before spraying, the electrode was heated to 700°C and as the coating was still porous they sprayed a second coating of manganese metaphosphate glass and a third layer of Cr_2O_3/aluminium polyphosphate gel. The authors observed (Vast - 1988) a reduction by a factor of 13 on the weight loss of the substrate with this multiple layer system.

iii) THE CONVERSION COATING - THE SILMOR PROCESS

An example of carbide conversion coatings generated on the carbon surface using the plasma arc spray technique was already described (Burykina - 1965). Another way of producing these coatings is using the Silmor process (Office National D'Etudes et de Recherches Aerospatiales - 1985) where the components to be coated are kept inside a reaction vessel, at 1800°C, above a mixture of silicon carbide and silica. At this temperature a silicon monoxide atmosphere is created and the following reaction takes place (Office National D'Etudes et de Recherches Aerospatiales - 1985).

$$SiO + 2C \rightarrow SiC + CO$$

It was shown that 1650°C is the lowest practical temperature at which conversion can take place, but at 1850°C however, the conversion is very rapid with 70% conversion within 5 minutes (Kleeping - 1986). Kleeping (Kleeping - 1986) verified that, during the oxidation tests of rocket nozzles, instead of the often observed cracking and spalling of CVD silicon carbide layer, the SiC surface layer applied by the Silmor process on graphite appeared to have failed in an alternative way with the damage confined to small pits at the leading edge of the nozzle. A C/C composite was also coated using the Silmor process and successful results were mainly achieved when a highly porous carbon-carbon matrix, subjected to single step densification procedure, was used (Office National D'Etudes et de Recherches Aerospatiales - 1985, Klepping - 1986).

iv) THE CHEMICAL VAPOUR DEPOSITION

This technique is possibly the most popular way of inhibiting the oxidation of carbon materials nowadays. It is, therefore, not a surprise that an impressive number of studies have been publishe in this area (Danis - 1981, Veltri[1] - 1984, Veltri[2] -1984, McKee[2] - 1984, Gray - 1984, Patten - 1985, Ryshkewitch - 1985, Johnson - 1986, Ehrburger - 1986, McKee[2] - 1986, Stinton - 1988, Kuroyanagi - 1990). The basic idea of this technique is to deposit a SiC or a Si_3N_4 coating on the carbon surface by chemical vapour deposition around 1600°C, after reaction between hydrogen and an organo-silicon compound, usually tetra ethyl ortho silicate (TEOS) or silicon fluorite, respectively. The single SiC coating produced using the CVD process offers inadequate protection for C/C composite materials, as noted previously, therefore, most modern coatings employ a CVD SiC refractory layer and a glassy layer to decrease permeability and to seal the cracks generated in the refractory coating (Johnson - 1986, Gray - 1984, Ehrburger - 1986, McKee[2] - 1984, McKee[2] - 1986, Kuroyanagi - 1990).

More sophisticated coatings consists of two different refractory layers, the first one being a conversion layer and the second one a CVD layer. Danis (Danis - 1981), for example, used two coatings of silicon carbide to improve the oxidation resistance of a gas turbine engine, the first one was a cemented SiC layer with a graded CTE and the second was a CVD SiC coating. Veltri (Veltri[1] - 1984, Veltri[2] -1984) published two patents for protective coatings applied on carbon-carbon

composites by chemical vapour deposition. The first one consisted of an initial SiC conversion coating applied before a pack SiC coating and a CVD Si_3N_4 coating applied after it (Veltri[1] - 1984). A single CVD Si_3N_4 coating was shown to be ineffective in reducing oxidation at 1093°C, since a weight loss of 5.8% occurred in 1 hour, while with the pack SiC coating (section v) the weight loss was 5.3% in 47 hours (Veltri[1] - 1984). A pyrolitic graphite layer, applied before the conversion coating reduced the weight loss to 5.5% in 165 hours (Veltri[1] - 1984). The second patent described the application of a CVD coating of SiC over the SiC pack coating (Veltri[2] -1984). Kuroyanagi (Kuroyanagi - 1990) protected C/C composites using a SiC conversion layer followed by a variation of the CVD process that was called pulse CVI, i.e., the gas mixture with 5% of CH_3SiCl_3-H_2 is pulsed into the reactor vessel, up to 720 Torr and held during 1 second when it is evacuated to below 3 Torr. These pulses are repeated 5000 times to infiltrate fine pyrolitic SiC into the microcracks of the conversion layer, but although there was some improvement in oxidation resistance provided by this sealing process, significant reductions in the weight loss were observed only when a glassy SiO_2-B_2O_3 layer was applied.

There have been other suggestions of potential refractory coatings, to be applied by the CVD technique, to improve the oxidation resistance of carbons, such as: Al_2O_3, ZrO_2, and pyrolitic carbon to combine the physical and mechanical properties of the individual phases (Stinton - 1988). A more complex suggestion was the use of carbides or nitrides of high atomic number transition metals, such as hafnium and zirconium to form stable oxides and provide protection to

carbon/carbon composites to temperatures approaching 3000 K (Patten - 1985, Ryshkewitch - 1985). About hafnium carbide especially it is convenient to bear in mind the results found by Suhoza (Suhoza - 1986) and summarized in the section vii.

v) PACK PROCESSES

This is the most successful technique in use nowadays to inhibit the oxidation of carbon material at high temperatures (around 1300°C) and is used to protect the leading edge of the Space Shuttle in the United States. The basic principle of producing a refractory coating on the carbon surface followed by filling its cracks with a glassy material is followed. The main difference between this technique and the others is the procedure used to generated both of these layers. Since 1979 when Curry (Curry - 1979) and Baker (Baker - 1981) published reports about this technique up to the review presented by Buckley (Buckley - 1988) several modifications were made and patents have been granted.

The aim of the process (Curry - 1979) consists in converting the outer surface of the carbon material to SiC, at the same time that an external refractory layer is generated, by mixing and packing around the component, in a segmented graphite retort, the following powders: alumina-10%, silicon-30%, and silicon carbide-60%. The retort is loaded into a furnace for a 16-hour cycle, which includes drying at 315°C followed by the coating reaction at 1650°C in argon atmosphere, when the outer layers of the carbon-carbon substrate are converted to

silicon carbide. This refractory layer is reinforced by impregnation with tetraethylortholisicate (TEOS) which, when cured, leaves a silicon dioxide residue throughout the coating and inside the microcracks. The coated, reinforced, carbon-carbon material is covered with a mesh, placed in a vacuum bag and impregnated five times with liquid TEOS and cured at 315°C, increasing the amount of silicon dioxide on the surface of pores and fissures, enhancing the oxidation protection of the carbon substrate. An internal NASA report (Rumler - 1983) mentioned the use of a low-temperature glass former to seal the refractory coating, already described (Curry - 1979), because it was verified that the oxidation of the silicon carbide coating formed a protective glassy SiO_2 layer only above 870°C.

The most substantial modification of the basic pack process was patented by Shuford (Shuford[1,2] - 1984). The proposed composition for forming a primary protective coating on carbonaceous substrate materials was about 25wt% to 40wt% particulate silicon, about 50% to 70% particulate silicon carbide, about 1% to 15% of particulate boron, by weight of the total composition, and a minor amount of magnesium oxide. The encased substrate and mixture were heated at higher temperatures than in the initial process, between 3175°F and 3350°F (1746°C and 1843°C), in an inert atmosphere, for a period of between about 4 and 7 hours to form the primary coating, about 125 and 750 μm thick. In applications where the coated substrate is to be exposed to cyclic temperatures, in which temperatures lower than 2500°F (1371°C) are also encountered, the same original impregnating procedure with TEOS was suggested, but followed by five applications

of a heat-cured slurry of an alkali silicate liquid and silicon carbide powder (weight ratio of 1:1) or a heat-cured monoaluminum phosphate solution, containing alumina and silicon carbide. A carbon-carbon composite substrate, with this enhancement coating was heated in air at 1000°F (538°C) for thirty hours and exhibited a net mass change of -0.0086 kg/m^2 of substrate surface area while at 2450°F (1343°C) the net mass change recorded was +0.017 kg/m^2 (Shuford[1] - 1984). A second patent presented, by the same author (Shuford[2] - 1984), introduced 22 parts, by volume, of 0.05N hydrochloric acid, as a catalyst, per 100 parts, by volume, of TEOS, when this material was applied to fill the microcracks of the refractory layer and a more detailed heat treatment for the alkali silicate-silicon carbide slurry is also suggested. To assure an improvement of the oxidation resistance of the C/C composite material TEOS impregnation was applied another five times after the alkali silicate - silicon carbide slurry. With this new procedure the weight loss exhibited by a coated sample was 0.0003 g/cm^2, in an oxidation test, at 1000°F (538°C) after 12 hours.

Except for two other works (Patten - 1985, Holzl - 1985) no more modifications were found in the literature for the pack processes. Patten (Patten - 1985) added to the material coated by the procedure described above (Shuford[2] - 1984) a layer of zirconium oxide, having a columnar microstructure, stabilized by calcium oxide, hafnium oxide, magnesium oxide, cerium oxide, ytrium oxide and mixtures thereof, with thickness between 50 and 130 micrometers that can be applied by plasma spraying or any other method. Holzl (Holzl - 1985) thermochemically deposited a silicon alloy coating in the form silicon carbide, silicon nitride, silicon oxynitride or a sialon on the C/C

composite surface. The exceptionally fine grain size and even grain distribution, in the coating, was employed to have a fine crack mosaic, minimizing the width of the cracks. At temperatures of the order of the melting point of silicon, or higher, silicon would flow in elemental form, or in the oxide form, weeping into the crack mosaic of the coating and forming an oxidation resistant glass filler. The use of a diffusion layer containing boron was recommended and it was preferably formed to a depth of at least 1 micron and up to 100 microns.

vi) OTHER METHODS AND TECHNIQUES

Iridium is a potentially useful substance to coat carbon materials and improve their oxidation resistance (section ii - The spray method) and the procedure used to apply a coating of this material by the plasma arc spray technique (Wright - 1968) has already been discussed. At least two other works attempted to produce a protective iridium coating on carbon materials by different ways. Criscione (Criscione - 1964), using multiple techniques, verified that iridium coatings applied by the dip method contained pores and pinholes and when dense, nonporous, adherent layers of Ir were obtained by a metal cladding method (electrodeposition and vapor plating) cracks were developed due to the difference in the thermal expansion between the coating and the graphite. Iridium was applied again (Macklin - 1967) on a very high CTE graphite ($8.1 \times 10^{-6}/^{\circ}C$ - temperature range 25 - $1650^{\circ}C$) to match the thermal expansion of the coating and the substrate, avoiding the problem observed by Criscione (Criscione - 1964). Six vapor deposition routes (Macklin - 1967), two fused salt electrolysis systems and four aqueous electrolysis systems were

selected for investigation. The following volatile iridium compounds were considered for vapour deposition: iridium hexafluoride, iridium trichloride, iridium acetylacetonate, biscyclopentadienyl iridium hydride, iridium trifluoroacetylacetonate, iridium tetrachloride and iridium tribromide. Iridium hexafluoride was considered the best choice for rapidly depositing iridium coatings. Graphite was precoated by thermal decomposition of iridium resinate and aqueous electrodeposition from iridium trichloride and sulfamic acid, to seal the pores, when a fused cyanide electrodeposition was then applied generating coatings as thick as 17mm. The oxidation tests were carried out using the induction heating technique and it was observed that a rather large initial weight loss occurred during the first 10 minutes and after that the weight loss rate was 52 $mg/cm^2/h$ at 2005^oC.

Coatings of nickel, titanium and aluminum oxide on C/C composite were obtained by electrochemical methods and was demonstrated their ineffectiveness as oxidation inhibitors (Rabotnov - 1978). The same work (Rabotnov - 1978) concluded that the application of silicon carbide to the reinforcing elements, at the same time as a film of boron nitride or silicon carbide to the surface of the composite, reduced the weight loss during oxidation.

In 1986, for the first time, a controlled hydrolysed sol was used (Sim - 1986) to produce ceramic alumina and zirconia coating on carbon-carbon composite. The alumina sol was prepared by hydrolysis of aluminum sec-butoxide while the zirconia sol was produced by hydrolysis of zirconium n-propoxide. In both cases excess of water was

used and the samples were dip-coated several times to produce a continuous coating. The oxidation protection did not seem to be promising: a weight loss of 67 mg/cm^2, in air at 1000°C after 10 min, was found for the uncoated sample, whereas a weight loss of 56-61 mg/cm^2 and 51-60 mg/cm^2 was observed for the alumina and zirconia coated sample, respectively.

Kaae (Kaae - 1988) studied the surface reactions of sealant materials with the objective of determining the critical interactions between the sealant glasses, i.e., alkali borosilicate glasses with viscosities between 10^2 and 10^3 poise over a temperature range 500-1200°C, used in oxidation protection systems for carbon-carbon composites, and the primary oxidation barrier coatings of silicon carbide or silicon nitride. Three ternary glass compositions with the ratio $Li_2O:B_2O_3$ equal to 1, were prepared by dry blending fine powders of lithium metasilicate, boric acid, silica and lithium carbonate. The slurry mixture was produced with methyl alcohol and after its evaporation the mixture was fused in air at 1000°C and held at temperature for 8-16 hours. It was observed that the leaching and hydration rate of the $LiO_2.B_2O_3.SiO_2$ glasses decreased sharply as the silica content increased to 50%. The wettability of these same glasses on Si, SiC and Si_3N_4 was measured by contact angle and it was observed that:

- ternary lithium borosilicate glasses wetted silicon, SiC and Si_3N_4 substrates and the contact angle increased with the increasing silica content of the glass;

- chemical reactions were observed between the glasses and the silicon substrates, and in some cases with the silicon carbide substrates;

- minimal interaction occurred between the glass and Si_3N_4;

- when the specimens were pre-oxidized to build up a silica film the contact angles tended to be lower and the interactions with silicon and SiC to be higher;

- for a pre-oxidized SiC substrate the glass tended to spread readily over it dissolving the silica film and increasing, consequently, the glass silica content. In this case the layer broke up into non-wetting beads.

I.2.3. - COMPARATIVE STUDIES

McKee (McKee[1] - 1986) compared the stability of powdered metallic borides, carbides, nitrides and silicides, towards oxygen, at temperatures up to 1000°C. He observed that the borides of Nb, Mo, V, W, Ti, Ta and Cr began to oxidise between 400 and 500°C and the products of their oxidation were nonprotective on the finely dispersed substrate particles. The borides of Hf, Ar and Al were somewhat more oxidation resistant, however at 1000°C they were substantially converted to oxide. The oxidation of Fe, Nb, Zr, Ti and V carbides was detectable at lower temperatures than that of the corresponding borides and the carbides of W, Fe, Zr and Ta were completely converted

to oxides below 1000°C. The thermogram for the molybdenum carbide showed a maximum weight gain around 850°C followed by sublimation of the volatile MoO_3 at higher temperatures. The oxidation of Cr_3C_2 was much less, at 1000°C, than that of the corresponding boride, apparently because the formation of a protective scale of Cr_2O_3. The conversion of the nitrides of Ta, Hf and V to oxides was also complete below 1000°C and the nitride of Mo was converted readily to MoO_3 which was volatile above 800°C. The nitride of chromium showed a very low susceptibility to oxidation with an apparent protective layer of Cr_2O_3. The silicide of Mo oxidized readily above 400°C and the silicides of Ti, Nb, Ta and Zr oxidized above 600°C. McKee (McKee[1] - 1986) also studied the effects of borides, carbides, nitrides and silicides on graphite oxidation kinetics and verified that : the borides, carbides and silicides of V and Mo and the carbide and silicide of W increased the oxidation rate; the borides of W, Zr, Cr, Si and Al decreased the oxidation rate; the carbides of Zr and Ta, the nitrites of Ta, Nb, Hf, Zr, Ti and the silicides of Nb, Hf, Zr exhibited little or no effect on the oxidation rate; TiC showed a slight catalytic activity, and $CrSi_2$ and CrN showed high levels of catalytic activity.

McKee (McKee - 1987) compared the oxidation resistance of C/C composites coated with a conversion SiC layer, using a boron oxide coating, to fill the cracks, with another using a silicon coating. It was verified that composite specimens coated with 50 microns thick layers of boron oxide showed negligible carbon gasification in 48 hours at 1000°C, in flowing dry air, and the fluidity of the coatings above 500°C provided protection against cracking during thermal cycling (McKee -

1987). It was demonstrated that a Si-C/C specimen which had been dipped in molten borate at 600°C showed no appreciable weight loss during the 20-hour experiment, but a similar specimen which had been coated only with silicon lost weight at a rate of 0.8%/hour on heating in flowing air at 1200°C (Figure 4) (McKee - 1987).

Strife (Strife - 1988) reviewed the state of the art for the inhibition of oxidation of carbon materials and some prominent studies were cited and briefly discussed while basic principles were emphasized. He stressed the importance of the glassy coatings and particularly the protective effect of boron oxide, liquid silicates and the sealant based on silicon ethoxide (Rogers[1] - 1976, Rogers[2] - 1976, NASA - 1981, Shuford[2] - 1984). Formulating the fundamentals for a good coating (Strife - 1988) it was suggested that: externally, it had to provide an effective barrier to inward diffusion of oxygen and had to possess low volatility; internally it had to have good adherence to the substrate without excessive penetration and prevent outward carbon diffusion or, at least, prevent carbothermic reduction of the oxides in the external layers. Ideally, one would prefer to use a material which formed an adherent in-situ oxide bearing in mind that the kinetics of oxide growth are substantially slower for the silicon-base ceramics than for aluminum-, hafnium-, or zirconium- based ceramic (Strife - 1988). Strife (Strife - 1988) divided the coatings for carbon-carbon composites in two main groups: coatings that aim to protect these materials up to 1800°C, based on SiC and Si_3N_4, and coatings for protection at higher temperatures. For temperatures above 1800°C Strife (Strife - 1988) suggested the use of a refractory oxide as an outerlayer, for erosion protection, and an inner layer to act as an

oxygen barrier and sealant for cracks in the coating, this inner layer would have to be isolated from the carbon substrate or carbide by a second layer of refractory oxide.

Suhoza (Suhoza - 1986) evaluated carbon-carbon composites for the orbit transfer vehicle (OTV). A series of hot-fire tests and long duration exposure to oxidation at temperatures up to 2,200°F (1204°C) were used to evaluate the eight nozzles produced by six different manufacturers. Four of these nozzles were uncoated, three of them were coated with silicon carbide and one was coated with hafnium carbide. It was concluded (Suhoza - 1986) that silicon carbide coating on low density material improved the oxidation resistance of the carbon-carbon composite while the hafnium carbide did not fully protect the substrate and permitted rapid oxidation of the low density carbon-carbon composite.

Different procedures of applying coatings on carbon-carbon composites, to improve oxidation resistance, were compared by Okamoto (Okamoto - 1986). The coatings were applyed in two steps. Firstly, the substrate was coated with SiC by three different processes: chemical vapor deposition, reaction process (the carbon on the surface of the C/C composite reacts with Si to produce SiC) and conversion process (the carbon on the surface of the C/C composite reacts with silicon-containing gas to produce SiC). The second step consisted of impregnating the surface with SiO_2 to close the microcracks in the SiC coating for all the processes used. Figure 5 shows that the mass loss obtained from the carbon-carbon composite coated with SiC was

smaller than that obtained from the uncoated substrate and there was not a large difference in mass loss among the three different processes. The results showed (Okamoto - 1986) that the mass loss decreased substantially by SiO_2 impregnation of the SiC-C/C (Figure 6).

Huetner (1988) compared various oxidation protections, for 2-D-carbon-carbon composites, with a base layer of SiC and additional B_2O_3 glasses treatment. The aim was long term protection, between 1500-1700K, for oxidation in air, including additional thermoshock resistance. The carbide forming processes included pack and slurry processes, impregnation with liquid silicon and CVD-processes. The results showed that pack processes, CVD coatings and combinations of Si-impregnation/CVD-SiC could be used as short time protection and the latter one exhibited the best thermoshock resistance. It was observed that all the protective layers on fine grained graphite were free of cracks, whereas the anisotropic 2D-C/C exhibited cracks and partly systematic crack patterns as a result of the different CTE between this carbon material and the SiC. The pack-processed samples presented an additional weight loss due to the burn-off of the fibre centers which had not been converted to SiC. The samples coated with coarse grained SiC showed a lower burn-off than the fine grained layer. After oxidation, only the samples protected by Si-liquid impregnation exhibited a smooth SiO_2 layer, i.e. without excess of elemental Si no SiO_2 formation seemed to be possible to seal the cracks and pores, fast enough, to avoid oxidation. When the SiC surfaces, formed during the pack processes, were glazed with B_2O_3, a considerable long term stability, over 100 hours under 80 l/h O_2-flow was observed.

Fitzer (Fitzer - 1988) compared two of the methods used to improve the oxidation resistance of carbon-carbon composites: the impregnation with silicon-organic compounds with subsequent thermolysis of the polymer to SiC and the direct chemical vapor impregnation with SiC from methyltrichlorosilane. For the liquid impregnation of the carbon-carbon composites, four silicon-organic compounds were used as SiC-precursor: 1.1.3.3-tetramethyl-1.3-disilacyclobutane, dodecamethylcyclohexasilane and two commercial products called Mark I (Yajima - 1975) and 020 (Munch - 1987). During the liquid impregnation process, the samples were evacuated and impregnated, under normal pressure with, the respective silicon-organic compound and thermally degraded at 1100°C in argon. The impregnation/thermolysis-cycle was repeated up to five times and the first two compounds required an autoclave treatment up to 600°C at 60 bar, in argon, prior to thermal degradation. For chemical vapor impregnation, the organic compound was applied under reduced pressure (p=150 to 400mbar, T=900 to 1000°C) with various Ar/H_2 ratios in a hot wall arrangement for 5, 10 and 15 hours. The oxidation attack was measured in a thermal balance during heating up to 1300 and 1600°C. After five impregnation/thermolysis-cycles with the commercial product 020 the open porosity was reduced from 21% to 5%, corresponding to a weight gain of about 240 mg. To achieve the same with the chemical vapor infiltration process, 5 hours were needed and the open porosity was reduced to 10-15%. Only after 15 hours of CVI, was the open porosity reduced, in the best cases, to 4-5%. The authors verified that the best oxidation resistance was achieved with

the samples in which surface coatings were formed additionally to the impregnation by CVI, especially after 15 hours of CVI treatment.

I.3 - SUMMARY AND CONCLUSIONS

The costs of improving the oxidation resistance of carbons are very high and vary largely, not only with the chemical substances used but also with the process. Technically the methods used to protect carbon materials, as well as the oxidation inhibitors applied are very closely related to the operating temperature and the heating and cooling procedures. Therefore, an optimum way to improve the oxidation resistance of carbons, in general does not exist; it is absolutely necessary to design the protective system for each individual application.

I.3.1 - INTERNAL PROTECTION

The mechanisms for the inhibition of carbon oxidation, in this case are usually the blockage of active sites, the substitution of carbon by more oxidation resistant materials and the deactivation of catalytic impurities present on the carbon surfaces.

It is well known that some common impurities, in the carbon products, act as catalysts of the oxidation reaction. It has also been recognized, since 1942, that it was possible to remove impurities from graphite using halogenous compounds, and some authors have proved that this procedure decreases the oxidation rate of the carbon materials.

The incorporation of chemical compounds into the constituents of the carbon articles has a double effect of generating gases that will purify them and/or blocking the active oxidation sites. The most successful materials used are zirconium, silicon, boron and phosphorus compounds. The phosphorus compounds are usually mixed with the raw materials while the others are incorporated, by several different ways, during the manufacture of the carbon articles. It is interesting to emphasize the importance of silicon and boron compounds on the oxidation resistance of the carbon materials and the degrading effect of alkali verified by Seegel (Seegel - 1981).

The new composite materials, produced by partial or total substitution of the carbon matrix in C/C composites, developed by Christin (Christin - 1980), Naslain (Naslain -1981) and several other authors have an improved oxidation resistance, if compared with the carbon-carbon composites and/or graphite, but they also have different thermal and mechanical properties. In this case also silicon and boron compounds were present in all the successful formulations.

All the internal protection methods should confer improved oxidation resistance to the carbon materials in air, but as pointed out by McKee (McKee - 1988), in the absence of an exterior impermeable coating the oxidation protection afforded at temperatures above 1000°C, by this method, is strictly limited. In a similar vein, Jawed (Jawed - 1986) affirmed that the best oxidation protection system should incorporate both matrix modification of the carbon-carbon composites and one or more coatings on the carbon surface.

I.3.2 - EXTERNAL PROTECTION

The impregnation method was possibly the first attempt to apply any oxidation inhibitor on the external and internal surface of the carbon material, not only because it is a simple way, but also because it is a well known technique in the carbon industry to densify the final product. It is interesting to emphasize that the most successful materials used are, again, silicon, boron and phosphorous compounds and that Baranski (Baranski - 1982) observed the same degrading alkali effect noticed by Seegel (Seegel - 1981) on carbon oxidation. The hydrophilic property of the glassy B_2O_3 coating and its degradative effect on the oxidation protection provided by this chemical compound was definitively proved.

The spray method comprises three different techniques, i.e., air spray, flame spray and the plasma arc spray. The air and flame spray techniques, are normally used to apply a molten metal and/or a

nitrocellulose lacquer slurry of a refractory substance or an oxide sol-gel on the carbon material. It is a very common method to protect electrode graphite and the most common substances used are aluminum, alumina, silicon and polyphosphate gels.

The plasma arc spray, well described by Baxter (Baxter - 1977), consists of applying a melted powder on the surface of the substrate and several trials were done with aluminum, nichrome, molybdenum, tungsten, titanium, zirconium, niobium, silicon, iridium, Al-Si, Ni-Si and alumina. The as-sprayed coating is porous and traps significant amount of oxygen, therefore several auxiliary techniques, such as vacuum spray, gas pressure bonding and remelting the coating have been applied, but there is no work published with successful results, at very high temperatures, using this technique.

Chemical vapor deposition is nowadays a well developed technique and a new area was opened (Stinton - 1988) with new metal-organic vapor sources. The substances applied are usually silicon carbide, silicon nitride, alumina and zirconium oxide. The disadvantages of the method are the difficulty in coating unusual shaped materials, the manipulation of hazardous organics substances at very high temperatures, around 1500^{o}C, the limitations on the size of the items to be coated, the time to produce a layer of protective thickness and the difficulty in developing a multilayer system using complex glasses or glassy-ceramic materials. In spite of these problems, this is the most widely used process, by the carbon producers, to inhibit the oxidation of graphites nowadays.

The conversion coating (Silmor process) is normally restricted to silicon carbide and, in the particular case of this refractory compound, it seems that this technique produces a coating with better mechanical compatibility with the substrate than the CVD method.

The pack process is certainly the most successful method to inhibit the oxidation of carbon materials, mainly carbon-carbon composites, at very high temperatures or during thermoshocks. Basically is a silicon-based system were the refractory coating is silicon carbide and the glassy coatings and sealants are silicates. It is a laborious method that requires specific equipment and a very long time to be completed.

Among the other methods and/or techniques it is convenient to highlight the work presented on the sol-gel method (Sim - 1986). In spite of the fact that there are some references to other technical works on this method (Fitzer - 1987, McKee[1] - 1986), just two reports (Vast - 1988, Sim - 1986) consider a chemically-controlled sols or gels applied to carbon materials.

I.3.3 - FINAL CONCLUSIONS

The principal points to emerge from this literature review are summarised in this section.

a) The protection afforded by the so-called internal protection methods is strictly limited without an external protective coating.

b) The most common substances used to provide an internal protection are boron and silicon compounds, particularly boron oxide and silicon carbide, and phosphorus compounds.

c) To inhibit the oxidation of carbon materials it is necessary to apply at least one protective surface coating.

d) The design of the protective system needed to inhibit the oxidation of the carbon material is strongly related to its final application.

e) The most successful refractory compound applied on carbon material has been silicon carbide. The main positive characteristics of this material are: chemical compatibility with carbon, a CTE that is one of the lowest found for refractory compounds, the silicon oxide barrier generated during oxidation in air, which has a low permeability to oxygen, and its availability and low price.

f) Silicon carbide, alone, can provide an effective protection to graphite up to moderate temperatures, but is ineffective at high temperatures or for protecting carbon-carbon composites.

g) To protect carbon materials at very high temperatures and specifically carbon-carbon composites it is necessary to use a multilayer system. The difference between the CTE of the refractory coatings and the carbon materials produces microcracks during the coating process or thermoshocks. These microcraks permit a catastrophic oxidation of the substrate.

h) To seal these microcracks, before they can be mechanically closed by the thermal expansion of the coating, it is necessary to apply at least one glassy coating. If just one glass coating is applied, it should melt around 500-700°C, but the ideal situation is to use successive layers, in accordance with the final purpose of the carbon material. Boron oxide is the most successful glassy coating applied up to the present, but it vaporizes around 1100-1200°C.

i) CVD is a technique capable of applying several different types of refractories compounds on the carbon surface but it is limited, for multilayer systems, by the costs and by the time necessary to reach an adequate layer thickness. Until now complex glasses and glassy-ceramic layers have not been applied yet using this technique.

j) The most successful external protective method is the pack process but it has severe limitations. It is a very laborious method and it is restricted to silicon systems which is limited to temperatures around 1600°C because of the carbothermic reduction of silicon oxide generating volatile silicon monoxide.

k) Two research areas are open, in fact, in the inhibition of the oxidation of carbon materials: the first is to find a more convenient, flexible and cheap method to build up the successive layers in the silicon-glassy system and the second is to develop another system and/or systems able to protect the carbon-carbon composites at temperatures above 1700°C.

It is clear from this survey that there are a number of avenues that are worth exploring in order to further develop effective coatings for control of oxidation of carbon materials. In the initial stages of this work it was decided to investigate the plasma arc spray method and the results achieved are presented in Chapter II of this thesis. This method was investigated from the late 1960s up to early 1980s (Criscione - 1964, Burykina - 1965, Elyutin - 1969, Kostikov - 1981, Konokotin - 1983, Alekseev - 1984) with inconclusive results but little work on this method has been carrried out in recent years. It was also concluded from the literature review that the sol-gel method was one which has received very little attention and yet offered great potential for future development. The sol-gel method is flexible, adaptable and also relatively inexpensive. The bulk of this thesis is dedicated to the

sol-gel method. A background about the sol-gel technique, the criteria for the layers choice, the selection of the glassy layers composition and the gels preparation are presented in Chapter III. The results achieved with this method are described in Chapter IV and discussed in Chapter V of this thesis. The conclusions of this work and suggestion for further research works are presented in Chapter VI.

CHAPTER II

THE PLASMA ARC SPRAY METHOD

II.1 - INTRODUCTION

Chapter I showed that the majority of works using plasma arc spraying were published in the seventies and no positive conclusion was established on the method's suitability as a coating method for inhibiting the oxidation of carbon materials. The literature review also showed that this technique has only being used to apply, on the carbon surface, iridium coatings, metallic coatings or metallic coatings to be converted to carbide. No evidence could be found of the application of the most successful materials in use nowadays, such as SiC.

Theoretically any potential substance, which does not volatilise, that it is able to inhibit the oxidation of carbon materials can be sprayed since the melting point of all refractory compounds and oxides is below the temperature of the arc produced in this equipment (15,000^{o}C) (Metco - 1988). The plasma arc spray has few limitations in coating different substrate shapes or sizes and as the facilities are available in the School of Materials Science, it was decided that an attempt to coat carbon materials, using this method, should be made.

II.2 - POSSIBLE COATINGS

All the refractory compounds (Samsonov - 1980) and oxides (Samsonov - 1973) regarded as promissing materials to produce a protective coating on carbons, with melting point higher than 2000°C, are listed below:

- refractory compounds

BeB_2, Be_2B_4, BeB_6, BeB_{12}, CaB_6, SrB_6, BaB_6, ScB_6, ScB_{12}, YB_2, YB_4, YB_6, YB_{12}, YB_{70}, LaB_6, CeB_6, PrB_6, NdB_6, SmB_6, GdB_4, GdB_6, TbB_4, TbB_6, DyB_4, DyB_6, ThB_4, ThB_6, UB_2, UB_4, UB_{12}, PuB, PuB_2, PuB_4, PuB_6, Ti_2B, TiB_2, ZrB_2, ZrB_{12}, HfB_2, V_3B_2, VB, V_3B_4, VB_2, NbB, Nb_3B_4, NbB_2, WBe_2, Ta_2B, TaB, Ta_3B_4, CrB, Cr_3B_4, CrB_2, Mo_2B, Mo_3B_2, MoB, MoB_2, Mo_2B_5, W_2B, WB, W_2B_5, WB_{12}, MnB_4, Re_3B, Re_7B_3, ReB_2, NiB_{12}, Be_2C, CaC_2, YC_2, LaC_2, CeC_2, PrC_2, NdC_2, SmC_2, ThC, ThC_2, UC, PuC, Pu_2C_3, PuC_2, TiC, ZrC, HfC, V_2C, VC, Nb_2C, NbC, Ta_2C, TaC, Mo_2C, MoC, W_2C, WC, Be_3N_2, ScN, YN, CeN, GdN, ThN, Th_3N_4, UN, NpN, PuN, TiN, ZrN, HfN, VN, NbN, TaN, Ta_2Al, Mo_3Al, RuAl, Ti_5Si_3, Zr_2Si, Zr_5Si_3, Zr_6Si_5, ZrSi, Hf_2Si, Hf_5Si_3, Hf_3Si_2, HfSi, V_5Si_3, Ta_2Si_3, Ta_5Si, $TaSi_2$, Mo_3Si, Mo_5Si_3, $MoSi_2$, W_5Si_3, WSi_2, Ba_3P_2, ScP, PrP, NdP, SmP, EuP, GdP, ThP, CaS, SrS, BaS, YS, LaS, La_3S_4, La_2S_3, CeS, Ce_3S_4, CeS_3, PrS, Pr_3S_4, NdS, Nd_3S_4, Nd_2S_3, ThS, Th_4S_7, US, PuS, B_4C, SiC, BN.

- oxides

Ta_2O_5, SiO_2, ZrO_2, HfO_2, Al_2O_3, BeO, CaO, Cr_2O_3, CeO_2, Ce_2O_3, MgO, MnO, NiO, Pr_2O_3, ThO_2, UO_2, Ac_2O_3, BaO, CoO, DY_2O_3, Er_2O_3, EuO, Gd_2O_3, Ho_2O_3, La_2O_3, Lu_2O_3, NbO_2, Nb_2O_3, NbO, NpO_2, PaO_2, Pa_2O_5, Pr_6O_{11}, RaO, Sc_2O_3, SiO, Sm_2O_3, SrO, TcO_2,

TiO, Ti_2O_3, TiO_2, Tb_2O_3, Tb_4O_7, ThO, Tm_2O_9, VO, V_2O_3, V_3O_5, U_2O_4, UO, Yb_2O_3, V_2O_3, Am_2O_3, PuO_2, MoO_2, Ga_2O_3, ZnO, Li_2O, Pr_2O_3, Nd_2O_3, Eu_2O_3, NpO_2.

The most important characteristic of a carbon coating, as previously discussed (chapter I), is to exhibit a compatible CTE value with the carbon substrates, not disregarding the fact that it should also be impervious to oxygen diffusion and be chemically compatible with the substrate. Ideally the range for coatings' CTE values would be between 1 to $7x10^{-6}/^oC$ and -1.5 to $1.5x10^{-6}/^oC$ for graphite and carbon-carbon composites substrates, respectively. Eliminating both the substances whose CTE values could not be found in the literature and those chemical compounds with CTE value higher than $10x10^{-6}/^oC$, the previous list of substances is reduced to:

- refractory compounds

CaB_6, SrB_6, BaB_6, YB_2, YB_4, YB_6, YB_{12}, NdB_6 SmB_6, GdB_4, GdB_6, TbB_4, TbB_6, DyB_4 ThB_4, ThB_6, TiB_2, HfB_2, VB_2, MoB_2, W_2B, CaC_2, YC_2, LaC_2, PrC_2, NdC_2, ThC_2, TiC, ZrC, HfC, Nb_2C, Ta_2C, Mo_2C, W_2C, WC, ThN, UN, TiN, ZrN, HfN, TaN, Mo_3Al, Zr_2Si, Zr_5Si_3, $ZrSi$, Mo_3Si, Mo_5Si_3, $MoSi_2$, B_4C, SiC, BN.

- oxides

Ta_2O_5, SiO_2, ZrO_2, HfO_2, Al_2O_3, Cr_2O_3, CeO_2, Pr_2O_3, TiO_2, Pr_2O_3.

Some of the refractory compounds listed exhibit a high oxidation rate at moderate temperatures (Samsonov - 1980, Storms - 1967,

McKee[f] - 1986) and some are radioactive. If these substances and Cr_2O_3, which is not compatible with carbon (Han - 1987), are disconsidered, the list of single materials suitable for coating a carbon substrate is now reduced to:

YB_2, YB_4, YB_6, YB_{12}, NdB_6 SmB_6, GdB_4, GdB_6, TbB_4, TbB_6, DyB_4 VB_2, MoB_2, W_2B, YC_2, LaC_2, PrC_2, NdC_2, ThC_2, ZrC, HfC, TiN, ZrN, HfN, Zr_2Si, Zr_5Si_3, ZrSi, Mo_3Si, Mo_5Si_3, $MoSi_2$, SiC, BN, Ta_2O_5, SiO_2, ZrO_2, HfO_2, Al_2O_3, CeO_2, Pr_2O_3, TiO_2, Pr_2O_3.

If the acceptable maximum CTE value is reduced to $6x10^{-6}/^{o}C$ and the chemical compounds already used to inhibit the oxidation of carbon materials are retained together with those whose CTE value was not found in the literature but are reported as compatible with the values for carbons (Strife - 1988) the new list of possible coating substances is reduced to:

HfC, Mo_5Si_3, SiC, BN, Ta_2O_5, SiO_2, ZrO_2, HfO_2, Al_2O_3.

Other substances, cited as promising materials in different research works, were included in this selection while Mo_5Si_3 and ZrTi were excluded because they are unavailable in the market leaving the final technological selection of potential coatings to be:

HfC, Mo_5Si_3, SiC, BN, Ta_2O_5, SiO_2, HfO_2, Al_2O_3, Si_3N_4, TaN, Si, HfTi, Cr_3C_2, ZrTi.

The cost of buying 300 cm^3 (Table 1), the minimal amount required for spraying, reduced the final selection of materials to be sprayed to SiC, Al_2O_3, Si, Si_3N_4, Cr_3C_2 and BN.

II.3 - EXPERIMENTAL

The plasma arc spray technique, described by Baxter (Baxter - 1977), involves the melting and subsequent deposition of a powdered material by means of a plasma arc. The equipment used was a Metco 3M plasma spray machine with argon, as the primary gas, and helium as the secondary gas. The arc power settings were varied between 50V/400A and 65V/450A in order to find satisfactory spray conditions. The powder feed unit was a Plasma-Technic 10C twin hopper unit. Powder was fed from the agitated hopper onto a variable speed metering wheel to allow variation of the powder deposition rate. The powder is carried to the plasma arc using argon as the carrier gas and fed into the arc via a number two nozzle. The sample was moved through the plasma arc on a computer controlled turntable which allowed variations of the traverse rate, the spray band width and the number of passes of the sample through the arc to be pre-programmed, thus ensuring an even powder distribution onto the substrate.

II.3.1 - SAMPLE PREPARATION

It was decided to start the development of the coating method

using electrode graphite as the carbon substrate. The price was the main reason for this decision although the optimized process was intended to be used for other engineering graphite grades and C/C composites.

A flat disc was assumed to be the most convenient shape for the samples in order to determine the spraying parameters of the different substances cited above and to optimize the spray conditions. Discs of 31.6mm were cut with the diamond saw, polished with coarse emery paper and cleaned with CCl_4. Their edges were machined to a radius of 1mm, using a lathe, to minimise the risk of failure of the coating at this critical feature (Figure 7).

II.3.2 - COATINGS

a) Ni-Cr-Al-Y

The first attempt to coat the carbon substrate was with Ni-Cr-Al-Y powder, normally used as a bond coating, supplied by Metco and with well-known spray conditions. The substrate was coated without any special preparation and despite the fact that a good pore penetration was observed (Figure 8), the results showed a very poor bond to the substrate (Figure 9).

Elyutin (Elyutin - 1969) and Baxter (Baxter - 1977) showed that there is a strong relationship between the carbon substrate temperature and the bond strength of the plasma-sprayed coatings.

Vast (Vast - 1988) also preheated graphite substrates up to 700°C; and similar recommendations are found in Metco's technical information (Metco - 1959). Consequently, it was decided to preheat the samples to 340°C, the maximum substrate temperature possible using the flame of the plasma arc spray apparatus. With this preheating an immediate improvement of the adhesion of the coating to the substrate was observed (Figure 10). Since then all the samples were preheated to this temperature prior to coating.

The spray conditions used for the Ni-Cr-Al-Y coating were:

traverse speed	- 0.5m/s
band width	- 4mm
nozzle distance	- 80mm
argon flow	- 80 SCFH at 50Psig/70°F
hydrogen flow	- 10 SCFH at 50Psig/70°F
voltage	- 60 - 65 volts
amperage	- 500 amps
powder port	- 2
powder feed rate	- 22%
carrier gas flow rate at 2.6 bar	- 45 cm^3/min

b) Al

As aluminium has been widely used as a bond coat in electrode graphite protection systems (chapter I), an attempt was also made to

spray this material, despite the fact that aluminium is not a convenient coating for high temperature purposes (Smialek - 1983).

The spray conditions used for the aluminium coating were:

traverse speed	- 0.5m/s
band width	- 4mm
nozzle distance	- 100mm
argon flow	- 150 SCFH at 50Psig/70^{o}F
hydrogen flow	- 5 SCFH at 50Psig/70^{o}F
voltage	- 65 volts
amperage	- 500 amps
powder port	- 1
powder feed rate	- 65%
carrier gas flow rate at 2.6 bar	- 40 - 45 cm^3/min

The coating exhibited very high porosity (Figure 11) and the spray conditions will have to be optimized if this substance is to be applied.

c) SiC

SiC was chosen to start the list of the selected coating substances because the literature showed that the majority of the successful systems inhibiting the oxidation of carbon materials are

SiC-based. However, all attempts to apply a coating of SiC on the carbon surface failed. The spray parameters such as nozzles, spray distance, feed rate, etc were changed without success. It seems that SiC alone is not a suitable compound for spraying, possibly because it decarburizes, or does not melt properly. If SiC really decarburizes this particular problem can be counteracted by including a hydrocarbon gas in the arc gases (Baxter - 1977), but if SiC is just heat-softened and not completely melted, in the plasma flame, as happens with tungsten carbide (Metco - 1959), the particles do not deform and flatten on impact, as with most other materials. In several attempts to spray SiC it was possible to observe its blasting effect, not only on the sample but also on the aluminium sample holder. It would appear that the powder does not melt properly.

d) Ni-Cr-Al-Y and SiC

In an attempt to find a carrier for SiC, Ni-Cr-Al-Y, which had been successfully sprayed, was used. The dual feed spray conditions used to spray this coating were:

Ni-Cr-Al-Y

traverse speed	- 0.5m/s
band width	- 4mm
nozzle distance	- 80mm
argon flow	- 80 SCFH at 50Psig/70^{o}F
hydrogen flow	- 10 SCFH at 50Psig/70^{o}F
voltage- 60	- 65 volts

amperage	- 500 amps
powder port	- 2
powder feed rate	- 15%
carrier gas flow rate at 2.6 bar	- 50 cm^3/min

SiC

traverse speed	- 0.5m/s
band width	- 4mm
nozzle distance	- 80mm
argon flow	- 80 SCFH at 50Psig/70°F
hydrogen flow	- 10 SCFH at 50Psig/70°F
voltage	- 60 - 65 volts
amperage	- 500 amps
powder port	- 2
powder feed rate	- 30%
carrier gas flow rate at 2.6 bar	- 50 cm^3/min

Only a very few particles of SiC were trapped in the Ni-Cr-Al-Y coating (Figure 12). These were identified using the X-ray mapping technique - EDX (Figure 13). Changes in the spray conditions did not improve the results.

e) Si, Si and SiC

It was thought that it would be possible to apply a Si coating or even to use the Si as a carrier for SiC and to promote its reaction on the carbon surface (Burykina - 1965) getting a uniform SiC coating.

The spray conditions to the Si and Si-SiC coatings were:

traverse speed	- 0.5m/s
band width	- 4mm
nozzle distance	- 80mm
argon flow	- 80 SCFH at 50Psig/70^{o}F
hydrogen flow	- 10 SCFH at 50Psig/70^{o}F
voltage	- 60 - 65 volts
amperage	- 500 amps
powder port	- 2
powder feed rate	- 25 - 30%
carrier gas flow rate at 2.6 bar	- 50 cm^3/min

These spray conditions produced a Si coating well bonded to the carbon substrate but exhibiting gross porosity (Figure 14). When Si was used as a carrier for SiC the same result as achieved with Ni-Cr-Al-Y was observed, i.e., only a few particles of SiC were trapped in the Si layer (Figure 15). A comparison between the weight gain of samples sprayed with Si and Si plus SiC (Table 2) showed that when SiC was mixed with Si (wt 50%) the weight gain % of the samples was only near

50% of the weight gain when Si was applied alone. It was, therefore, verified that SiC was not carried by Si on the surface of the sample, but wasted.

f) Cr_3C_2

Following the list of possible substances suitable for coating carbon materials, the next trial was with Cr_3C_2.

The spray conditions were:

traverse speed	- 0.5m/s
band width	- 4mm
nozzle distance	- 80mm
argon flow	- 80 SCFH at 50Psig/70°F
hydrogen flow	- SCFH at 50Psig/70°F
voltage	- 60 - 65 volts
amperage	- 500 amps
powder port	- 2
powder feed rate	- 30%
carrier gas flow rate at 2.6 bar	- 50 cm^3/min

It is possible to verify (Figure 16) that just few particles of Cr_3C_2 were deposited on the surface of the graphite. The work presented by Wuest (Wuest - 1985) suggested that chromium carbide

has not been applied singly but with 25% of NiCr used as a carrier.

II.4 - CONCLUSIONS

a) It was verified that few of the most common refractory materials and oxides were able to satisfy the basic precondition for protecting carbon materials - very low CTE value - and that the most sophisticated substances would have a prohibitive cost when applied by this method due to its relatively low efficiency.

b) The coatings applied on preheated carbon samples showed better adhesion to the carbon substrate.

c) Between the six substances selected for spraying onto carbon surface, three were tried but just one coating could be considered satisfactory (Si). SiC which is recognized as one of the most successful refractory materials used to inhibit the oxidation of carbons could not be sprayed at all and the use of any carrier will probably adversely affect its carbon protection properties.

d) All the coatings that have been sprayed showed a very high porosity. This fact leads previous works, using this particular method, to introduce other sophisticated techniques, e.g. gas pressure bonding (Chapter I), to overcome this problem.

e) It is therefore assumed, considering the results achieved and the literature review (Chapter I), that it would be very difficult to produce a protection system capable of inhibiting the oxidation of carbon materials, at very high temperatures, using this method.

CHAPTER III

THE SOL-GEL METHOD

III.1 - INTRODUCTION

It was concluded in Chapter II that it would be very difficult to produce a protective coating to inhibit oxidation of carbon materials using the plasma arc spray method. Therefore the bulk of the work reported in this thesis is devoted to the development of coatings using sol-gel methods. The physico-chemical principles of the sol-gel methods for the production of ceramic artefacts, including coatings, are reviewed in this chapter in Sections III.1 to III.6. This review provides criteria for the selection of sol-gel routes for the development of multilayer coatings on carbons which are presented in Section III.7. Experimental details for the preparation of the sols and gels are described in Section III.8.

All the known refractory compounds and oxides have higher CTE value than carbon, as shown in the previous chapter and, therefore, it is difficult to inhibit the oxidation of carbon materials with just one of these chemical compounds as a coating. During the cooldown, after the protective refractory coating was applied or even during thermoshocks, microcracks are developed in it and they will allow a catastrophic oxidation of the substrate to take place. The reviewed literature on coatings, chapter I, showed the necessity of using multilayer systems and the benefits of including glasses in them to fill these cracks and enhance the oxidation protection. This was particularly necessary for carbon-carbon composites because their CTE

values, sometimes negative, exhibit larger mismatch with the CTE of the potential protective coatings than graphites.

The ideal glassy coating, to integrate a multilayer system, should melt around 500°C, when the refractory coating's microcracks are not yet mechanically sealed and the oxidation reaction starts. It should also have low permeability to oxygen, acting as a diffusion barrier, and its volatilization should not start below 1600°C to permit the carbon materials to be used at least at this temperature. Since a glass or glass-ceramic with these properties could not be found in the literature, it was thought that layers of different compositions should be applied in order to confer the required physico-chemical properties to the system.

SiO_2 is a basic material for most glasses produced nowadays, it has a low CTE, low permeability to oxygen diffusion and it is the oxidation product of a refractory SiC layer. The limiting temperature to a SiO_2 layer applied on carbon, and consequently the use of SiC as a protective refractory coating, is around 1600°C when the $Si0_2$ is reduced by carbon and the SiO generated is volatilized (Wright - 1968, Naslain - 1981, Strife - 1988). Unfortunately SiO_2 only melts around 1800°C when it really becomes a protective coating. B_2O_3, exhibiting melting point around 450°C, has been in widespread use to seal microcracks in refractory coatings and therefore enhance the oxidation protection at low temperatures. The volatilization of B_2O_3 is around 1100°C and, therefore, it can not be considered as a convenient option when the operating temperature of the carbon material is above this value. It is, therefore, necessary to search for glassy or glass-ceramic

compositions, able to fulfil all the requirements cited above and to develop their production and application technique on carbon materials.

Glasses and the glassy materials are traditionaly produced by melting and quenching the appropriate oxide composition or, more recently by the sol-gel technique. SiC particles have also been claimed to be produced by sol-gel techniques in several publications (Wei - 1984, Fox - 1986, White[1] - 1987, White[2] - 1987, Chen - 1988, Park - 1988, Sugahara - 1988,). The possibility of developing a protective multilayer system for the carbon materials by the sol-gel technique, generating both refractory and glassy/glass-ceramic coatings, appeared to be promising. The potential technical and economical advantages of this technique, for this particular application, over any other industrial process in use nowadays, are evident. No special equipment is needed and consequently no large initial investment is required. The high reactivity of the gels, that facilitates reactions at lower temperatures (Figure 17), will reduce the costs in generating a protective coating. Lastly there is no method able to compete in versatility with the sol-gel technique to produce complex and varied formulations of glassy/glass-ceramic coatings.

III.2 - GENERALITIES

The sol-gel process is essentially a chemical route to obtain high purity inorganic materials. It is possible to synthesize these materials

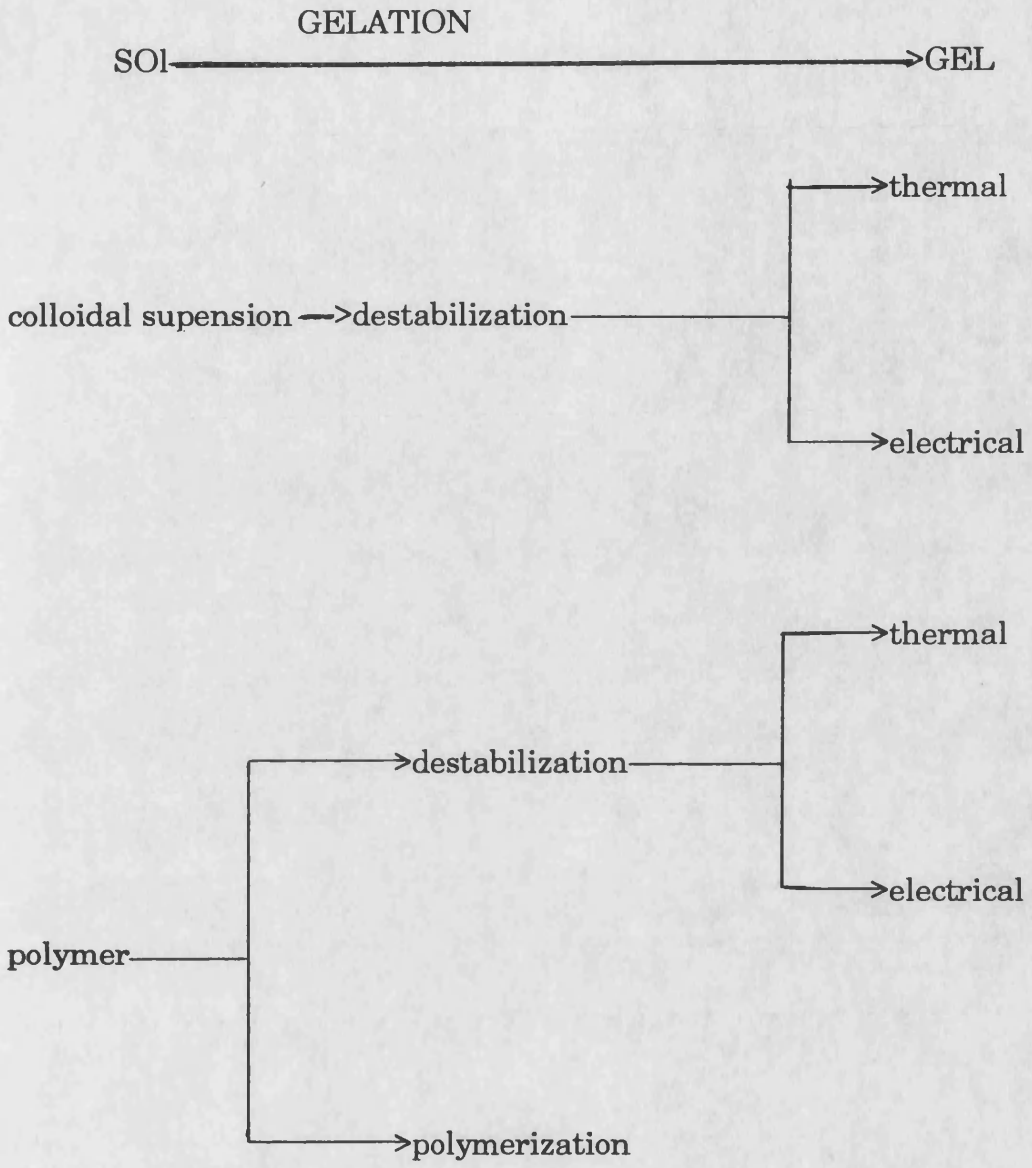
in a variety of forms including: near net shape monolithic components, powders as precursors in the production of ceramics, fibres and whiskers, thin coatings with various optical characteristics, etc (Jones - 1988). It also provides an easy way to purify the precursors and to get pure products with a molecular level of homogeneity in multicomponent materials. It permits the use of chemistry to control the reactions involved and in consequence a high and accurate level of manipulation of the characteristics of the products (Schmidt - 1988, Sakka - 1987).

The use of the sol-gel method in preparing glasses and ceramics is not new, in fact Thomas Graham carried out investigations of silica gel as early as 1864. The potential advantages of the sol-gel method for glass products are probably exploitable for "speciality" items and for special fabrication where costs are relatively unimportant (Mackenzie - 1984). In the case of coatings and films, the costs of raw materials are relatively insignificant, and the sol-gel method is therefore attractive and the potential for increasing applications should be excellent (Mackenzie - 1984).

One of the problems of development of new applications for the sol-gel method is the lack of scientific understanding (Mackenzie[1] - 1988) mainly for the reactions mechanisms and the effects of all parameters on the final properties of products. At present, the science of the sol-gel method is still in its infancy (Mackenzie - 1986).

The words "sol-gel" refer to two physico-chemical states of the system which arise during the process. The sol is a colloidal suspension of particles, whose diameters are usually below 100nm, prepared by mechanical or electrical dispersion of the materials in a solution which is only just stable. Sols may also be created by polymerization of lower molecular weight species in solution which grow until again they are also only just stable (Jones - 1988, Partlow - 1981)

There are, therefore, two ways of obtaining gels: destabilization of a sol or pure hydrolysis and polycondensation of organometallic compounds. Destabilization can be achieved by thermal particle agitation or change in the electrical particle charges, by electrolyte addition, while hydrolysis and polycondensation are nothing else than polymerization.



The sol-gel transition should be distinguished from a precipitation (or flocculation) mechanism in which separate aggregates are formed, in contrast to the continuous three-dimensional particle networks (Figure 18). There are fundamental differences in the natures of the gels formed by these two mechanisms, i.e. colloidal suspension or polymerization. In a colloidal system the gelling point is simply an indication of the interparticle distance where the charge interaction is strong enough to arrest the transitional motion of colloids (Yoldas - 1984). This interaction may affect the integrity and porosity

of the materials; however, it hardly influences the fundamental properties (Yoldas - 1984). In polymer systems gelling occurs as an extended polymer network forms, or by destabilization of adequate size molecules, and in these cases structural variations can be introduced in the gel to modify its properties and to tailor the final gel-product to its application. Most work in the sol-gel field has been performed recently by polymerization and condensation of organo-metalic compounds using alkoxides as precursors (Schmidt - 1988). The alkoxide route is normally preffered for special applications because the process, the structure of the gels and their properties can be easily controlled by controlling hydrolysis and condensation rate by chemical means.

The reactions leading to oxide network and gel formation through the alkoxide route can be represented by:

$$\equiv M\text{-}OR + HOH \rightarrow \equiv M\text{-}OH + R(OH) \qquad (6)$$

$$\equiv M\text{-}OH + HO\text{-}M\equiv \rightarrow \equiv M\text{-}O\text{-}M\equiv + H_2O \qquad (7)$$

$$\equiv M\text{-}OH + RO\text{-}M\equiv \rightarrow \equiv M\text{-}O\text{-}M\equiv + ROH \qquad (8)$$

(6) - hydrolysis

(7), (8) condensation or polymerization

The parameters that introduce structural variations in polymer gel network are, consequently:

1. Kinetics of hydrolysis and polymerization reactions, affected by: starting alkoxides, water/alkoxide ratio and water addition, amount and type of solvent, amount and type of catalyst and reaction temperature.

2. Order of reaction in multicomponent systems.

3. Gelling and ageing temperatures.

Figure 19 illustrates schematically the gel structure obtained from an acid catalysed hydrolysis, a base catalysed hydrolysis, an aged colloidal gel (a gel where the atom bondings were strenghtened by drying or heating) and a weakly bonded colloidal gel. It is possible to verify the range of structures obtainable through the alkoxide route (Figure 19A and 19B) in comparison with the colloidal route (Figure 19C and 19D).

Apparently this is a straight forward technique as the alkoxides are soluble in a variety of organic solvents, specially alcohols but in reality both reactions, i.e. hydrolysis and condensation, are not separated in time, but to significant degree they take place simultaneously and it is essential to control and minimize precipitation if high quality products are to be manufactured. Precipitates in alkoxide solution can be produced by either a chemical reaction or a physical agglomeration, i.e. when the reaction product is insoluble or slightly soluble in the host solvent or when the saturation limit of a solute is reached. It is possible to eliminate the production of these

precipitates by changing the temperature, the pH of the solution, the water concentration, the mode of water addition and modifying the precursors to decrease its hydrolysis degree and rate (Zheng - 1988).

The preparation of glass and/or glass-ceramics, through the sol-gel route, can be divided in three stages of which gel synthesis is only the first. The others, equally important stages, are drying and gel-glass or gel-glass-ceramic conversion. The drying process is perhaps the most critical step in producing monoliths using the chemical route. The drying of a structure with very high surface area, like a gel, is difficult and leads to mechanical breaking of the gel body if special techniques are not applied. The amount of liquids (water and solvent), trapped by the gel is, between 40 and 70% (Klein - 1984), and its removal, without breaking the piece, is normally the main problem to be overcome. Not only the drying speed but the desirable high gel density (Schmidt - 1988), the pore size and pore size distribution in the gel are also strongly related to the cracks produced.

The drying speed can be controlled physically or chemically. Physically reducing the exposed area to the gel in contact with the atmosphere, trying to keep the weight loss below 10% per day (Klein - 1984), or using hypercritical evacuation for the liquid mixture trapped in the gel or a deep freeze technique. Chemically the drying speed can be controlled by the use of additives such as formamide, glycerol, etc. These additives will also affect the pore size and pore size distribution that are also factors responsible for the cracks generated during drying.

The third stage is the gel-glass or gel-glass-ceramic conversion that requires further heating. Densification of the gel-derived amorphous solids can frequently be accompanied by crystallization (Mackenzie - 1988). The weight loss during firing is around 25% (Klein - 1984) and again the porosity is an important factor in obtaining a bulk piece.

Except for the relatively old and established application of alkoxide gels to thin films deposition no other industrial application of the sol-gel processes is known yet but the potentialities of the method are enormous (Rabinovich - 1985). As an example, a fully dense Mullite was obtained at 1200°C (Ulrich - 1988), by the sol-gel technique instead of the conventional melted which involves firing to 1600°C (Figure 20). The sol-gel product exhibited higher flexural strength and no strength decrease at least up to 1400°C, because the scale of chemical uniformity approaches the molecular level (Figure 20). Another example is shown in Figure 21 where two high temperature ceramics, with near zero expansion, have also been produced by the sol-gel method, and one of them, $Ca_{0.5}Sr_{0.5}Zr_2P_6O_{24}$, is claimed to keep its mechanical properties up to 1700°C (Ulrich - 1988).

III.3 - THE EFFECT OF THE PARAMETERS ON THE GEL STRUCTURE

III.3.1 - CATALYST

The catalyst is certainly the most important parameter to determine the structure and the properties of a gel because it affects the relative rates of hydrolysis, condensation and polymerization more than any other parameter such as e.g. the water/alkoxide ratio. The most dramatic structural differences appears between acid and base-catalysed gels but between the acids themselves structural differences can be noticed.

The most commonly proposed mechanism for base-catalyzed gels is nucleophilic attack on silicon (Brinker - 1982).

$(RO)_3SiOH + OH^- \rightarrow (RO)_3SiO^- + H_2O$ (9) (fast)

$(RO)_3SiO^- + (RO)_3SiOH \rightarrow (RO)_3SiOSi(OR)_3 + OH^-$ (10) (rate determining)

Brinker (Brinker - 1982) proposed that at high pH the extent of reaction (9) increases with the acidity of the Si atom at $(RO)_3SiOH$, due to electronic effects, when the dimer, $(HO)_3SiOSi(OH)_3$, is formed. Moreover, the more extensive the cross-linking in $(RO)_3SiOH$, the more the acidity of the remaining silanol groups increases. Thus, in a solution of polymers of various degrees of cross-linking, the more cross-linked species will be the most likely to undergo reaction (9) and be available for reaction (10) (Brinker - 1982). The base-catalyzed gels are

characterized by low dry densities which vary more with amount of base than amount of water (Klein -1984, Brinker - 1985).

An alternative situation occurs when the rate of condensation of silanols is greater than their rate of their production by hydrolysis. This occurs during acid catalyzed hydrolysis, mainly at low water and high acid concentrations. The acid catalyzed hydrolysis proceeds by a mechanism which involves electrophilic attack on an alkoxide oxygen (Brinker - 1982) and the following sequence is preferred: monomers, end groups of chains, middle groups of chains.

$(RO)_3SiOH + H_3O^+ \rightarrow (RO)_3SiOH_2^+ + H_2O$ (11) (rate determining)

$(RO)_3SiOH_2^+ + (RO)_3SiOH \rightarrow (RO)_3SiOSi(RO)_3 + H_3O^+$ (12) (fast)

The resulting polymer, therefore, is relatively small, not highly cross-linked and exhibits a high dry density, large specific surface area and a small mean pore diameter. The density decreases with increasing water/alkoxide ratio in the original solution as a consequence of the increase of the cross-linking effect, due to the higher hydrolysis rate, equation 9. More weakly cross-linked gels, i.e. acid-catalyzed gels, exhibit greater shrinkage and crack generation in response to surface tension forces than more highly cross-linked gels, i.e. base-catalyzed gels, (Brinker - 1984, Prassas - 1984, Maniar - 1988) and in consequence their thermal conversion into monolithic glasses, although achieved with lower temperatures (YU - 1982), are usually more difficult.

Although these mechanisms are still widely accepted to explain the effect of the catalyst on the gel structure, one can observe (Table 3) that the bulk densities of the HF and NH_4OH catalyzed gels are significantly lower than those of the four other gels in both the heat treated and not treated samples, indicating that the HF catalyzed gels appear to exhibit similar structure to the NH_4OH catalyzed gels (Pope - 1986).

The catalyst concentration also plays an important role on the gel structure, although its influence is much less than the type of catalyst itself. However its effect, for HCl catalyzed gels, on the gelation time, apparent density and porosity, Figure 22, still shows its remarkable influence on these properties.

III.3.2 - WATER

After the catalyst, the amount of water is possibly the most important parameter to be considered when a gel or any final gel-derived product is to be tailored. Once the catalyst is chosen, the type of polymers formed during hydrolysis, i.e. whether they will present longer linear chains or higher cross-linked networks, depends on the water/alkoxide ratio used. The progress of polymerization, for silica gels made from tetraethylorthosilicate under acidic conditions, as a function of the amount of water is showed in Figure 23. The peaks, in this figure, represent the quantity of Q2, Q3, and Q4 species, Qn being

the fraction of Si atoms bonded through oxygen to other Si atoms; thus, Q0 is a monomer and Q4 is Si surrounded by 4 bridging oxygens. All of the solutions gelled in less than 12 h, but the degree of cross-linking (i.e., the average value of n) is much greater in the gels made with larger amount of water (Scherer - 1988).

As the water/alkoxide ratio increases the oxide content increases (Yoldas - 1982), Figure 24, and as long as the ratio is larger than 4, the dried gels are free of most of the organic compounds after heat treatment (Klein - 1984). However, the water/alkoxide ratio should be greater than 10 for the dried gel to densify without cracking (Klein - 1984). This may suggest that the excess water has a dual effect, first on the porosity assuring a minimal pore size diameter for elimination of the organics during the heat treatment, so pores can shrink, and second to encourage cross-linking to form a tighter network (Klein - 1984, Sakka - 1980). In other words, some minimum number of cross-links must be formed to permit drying and firing of monoliths in a reasonable amount of time without cracking.

The relationship between the degree of cross-links and wettability was indirectly studied by Butts (Butts - 1988) who identified three types of wetting behavior in accordance to the water/alkoxide ratio (Figure 25).

Type I - the sol initially wets a small area of the substrate that withdraws to form a single bead, which remains until gelation after several minutes.

Type II - the sol initially spreads over the substrate then withdraws from macroscopic areas, generally from the circumference of the coating but also from a few isolated regions within the previously wetted region.

Type III - the sol spreads uniformly, rapidly and extensively over the substrate.

It was observed that high acid contents essentially eliminated the differences between the three wetting behaviors, but at standard acid levels (0.002mol/1mol TEOS) the water content plays a role (Butts - 1988). Low water content sols (2.5 mol water/mol TEOS) typically give type I wetting influenced by unhydrolyzed alkoxides; medium water contents (5 mol water/mol TEOS) yield good coatings of type III wetting and high water contents (10 mol water/mol TEOS) yield type II coatings. It was not explained why the coating quality tended to maximize at the intermediate water contents (Butts - 1988).

The water addition rate should also be considered very carefully, since it is an important parameter closely related to the homogeneity of the gel (Schmidt - 1988).

III.3.3 - SOLVENT

Another way of interfering with the gel structure is certainly through the type and amount of solvent. These parameters affect the movement of the molecules and consequently those reactions which

depend on the diffusion of larger species, such as polymerization (Yoldas - 1982). Consequently, the polymer size, as well as the oxide content, should decrease and the gelation time should increase when the concentration of the solvent and its molecule size increases.

It was suggested that the amount of solvent lost during gelation must have a significant influence on the bulk density of the gel and hence its porosity and probably the average size of the pores (Mackenzie - 1986). The specific surface areas of SiO_2 gels, using C_2H_5OH, CH_3OH and n-C_3H_7OH as solvents, were measured by Mackenzie (Mackenzie - 1988) as 169, 385 and 305 m^2/g and such differences were partially attributed to the specific volume and the vapor pressure of the solvents.

III.3.4 - ADDITIVES

Stresses are normally built up in the gel, during drying, leading to severe cracking. This effect can be minimized by tailoring the gel structure to obtain larger pores and uniform pore distribution and/or by slow drying or improved drying techniques such as hypercritical drying or deep freezing. Uniform pore distribution in the gel and lower drying speed, can be achieved by the addition of drying control chemical additives (DCCA) such as formamide (NH_2CHO), glycerol ($C_3H_8O_3$) and oxalic acid ($C_2H_2O_4.2H_2O$), during the sol preparation.

The chemical mechanism used by DCCAs to affect the gel structure are not yet well explained. For example, formamide and oxalic acid produce larger and more uniform pores (Scherer - 1988).

Other authors (Ulrich - 1988, Hench - 1986) demonstrated (Figure 26) that formamide produces a large sol-gel network with uniform large pores but an acidic DCCA, such as oxalic acid, results in a somewhat smaller scale network with a narrow distribution of pores (Figure 27).

There are no doubts, however, that the addition of DCCAs improves the strength of the gel, making it better able to resist capillary stresses (Scherer - 1988) and that the low vapor pressures of formamide and glycerol allow the other solvents (typically alcohol and water) to evaporate more rapidly, creating a concentration gradient of solvent in DCCA (Scherer - 1988). Since interdiffusion of liquids is rapid, the solvent can be removed from the interior at almost the same rate that it evaporates from the surface (Scherer - 1988) and as a result, the shrinkage of the gel is more uniform and consequently the warping and drying stresses are minimized.

Another important controversy about formamide DCCA addition to sols during the gel manufacture is related to its effect on the hydrolysis reaction. Artaki (Artaki - 1986) found that formamide hinders the hydrolysis reaction and possibly favors the condensation of incompletely hydrolyzed species, thereby entrapping a larger percentage of alkyl groups in the Si polymers of the sol. Hench (Hench[2] - 1986) suggests that formamide DCCA markedly decreases the rate of hydrolysis and increases the rate of condensation. In both hypothese a larger and more highly branched but less dense SiO_2 network should be formed.

III.3.5 - PRECURSORS

The starting compound has an important influence on the hydrolysis product, with the rate of hydrolysis being affected by the steric and electronic effect of the alkyl groups of the alkoxide. In some extreme cases, Table 4, a transparent and homogeneous gel could not be produced. When a homogeneous gel was achieved, the gelation time was higher for the alkoxides with larger molecular volumes while larger polymer units and consequently higher oxide contents were obtained from those with lower alkyl groups, Table 5, (Yoldas - 1984, Chen - 1986).

The solubility of the precursor is another factor to be considered during the gel preparation, and the results (Prassas - 1984) showed that tetramethoxysilane (TMS) and tetraethoxysilane (TEOS) are only slightly miscible with water and their corresponding alcohols, however, TMS can be used in more concentrated solution than its TEOS homologue.

III.3.6 - TEMPERATURE

High temperature in the host medium (60-70^{o}C), during the gel manufacture, facilitates diffusion and leads to the formation of larger polymers with higher oxide contents (Yoldas - 1984) and larger porosity which will facilitate the vaporization of volatile substances, such as solvents and water (Sakka - 1987).

III.4 - DRYING PROCESS AND DENSIFICATION

DRYING PROCESS

The production of a gel is followed by aging and drying. Aging means that the network of particles is strengthned by a mechanism involving the partial coalescence of the particles leading to a thickening of the neck (Figure 28) (Zarzycki[1] - 1984), and drying means the elimination of the volatile compounds. A gel can be aged without drying, but during drying the aging process is unavoidable and this is the most delicate step in producing monoliths from gels (Prassas - 1984).

The freshly prepared gel is formed of a network of particles holding an interstitial liquid - the solvent trapped during the gelling step, water in the case of hydrogels (gel by destabilization) or mixtures of alcohols and water for the alcogels (gel from alkoxide) (Zarzycki[1] - 1984). Elimination of these liquid phases leads to dry gels, therefore, drying is connected with shrinking due to the elimination of water, solvents and additives, when used.

Strains appear during drying and, if they cannot be stopped by relaxation, cracks appear. The liquid phase concentration gradient (which is the driving force for liquid transport) leads to surface tensile stress and cracks begin to propagate from the surface, a very common

observation during gel drying (Figure 29). The chemical (or physical) interaction of liquids with the pore walls is one of main causes of the capillary forces and the stress formation and is dependent on: pore size (small pores are more efficient for interaction than large ones), temperature (increases diffusion without increasing capillary forces), the chemical state of pore wall (number of OH groups or number of other hydrophilic groups), pore shape and interconnection (cylindric shape, bottle necks) (Schimdt - 1988).

The control of undesirable cracking of gels during the drying stage can be achieved by: 1) strengthening the gel by reinforcement and/or ageing, 2) enlarging the pores, 3) reducing the surface tension of the liquid, 4) making the surface hydrophobic, 5) operating in hypercritical conditions, 6) evacuating the solvent by freeze-drying (Zarzycki - 1982). The drying of thin gel films on solid substrates usually presents no particular problems owing to the large surface of evaporation compared to the thickness of the layer (Zarzycki2 - 1984). So far, the most successful results during drying have been achieved by reduction of the cappillary forces, by enlarging the pores and by reduction of the surface tension by using surfactants or hypercritical drying (Zarzycki2 - 1984). In fact, comparative analysis between aerogels (gels produced by hypercritical drying) and xerogels (gels dried in air) demonstrated that just the first produces pores of uniform size with diameter around 15nm (Iura - 1988)).

DENSIFICATION

After that the gel is produced and dried, all the structural properties are already defined. The conditions necessary to promote the gel-glass or gel-glass-ceramic conversion, e.g. the sintering temperature, will be related to the structural properties of the dried gel. The main point at this stage is certainly the pore structure left behind during drying. Densification is essentially a sintering process by which the pores of a dry gel are eliminated and the material converted into clear, massive glass or glass-ceramic piece (Zarzycki - 1982).

A sucessfull gel-glass or gel-glass-ceramic conversion is closely related to the firing procedure, the heating rate, as well as the crystallization parameters that should be considered for each particular case and composition. Low density gels, such as base-catalysed gels, require higher temperatures to be densified (Iura - 1988) while high density gels, acid-catalysed gels, can crack more easily during densification.

III.5 - FILMS AND COATINGS

Thin films may be deposited from the sols and gels, at room temperature, and cured to form glassy coatings at relatively low temperatures by brushing, dipping and spinning techniques (Sakka - 1987, Mukherjee - 1984, Scriven - 1988) or even by thermophoretic deposition (Dalzell - 1986). The coating of metal, plastic and glass

substrates with metal alkoxides solution is attracting a great deal of attention because it enables new functions for the substrate or improves its surface characteristics changing optical, mechanical or electrical properties (Sakka - 1984, Orgaz - 1986). As the gels have very high surface free energy and will try to reduce this energy it is possible to sinter a coating at quite a low temperature. Dilute solutions, of 1-6 cP in viscosity, are normally used for obtaining uniform coating films which firmly adhere to the substrate (Sakka - 1984) leaving a final thickness below 0.5 microns (Orgaz - 1986, Strawbridge - 1986). Polyether glycol (PEG) added to SiO_2-B_2O_3 sol (Tohge - 1988) increased viscosity of the coating solution and the thickness of the as-coated films, delayed the gelation time (Figure - 30) and improved the coating quality.

Sol-gel derived tantalum oxide films were applied on glass multiple layers up to 300nm thickness. While unfired films were easily scratched and could be removed from the substrates by scraping, films heated to a temperature as low as 150°C were not removed or damaged by limited physical abrasion (Silverman - 1986). Thick films often separate from the substrates on drying and heating, probably because a high mechanical bending stress was caused in the film as a result of the non-uniform shrikage and the largely differential shrinkage between the top surface of the film and the bottom surface attaching to the substrate (Sakka - 1980). It is thought that excellent coating films are obtained when the bonds between film and substrate can be produced before strong bonds within the film are formed (Sakka - 1984, 1987).

III.6 - HYDROLYSIS RATE - MULTICOMPONENT SYSTEM

When multicomponent systems are to be prepared, i.e. when more than one alkoxide is to be used to produce a complex glass or glass-ceramic material, the rate of hydrolysis and polymerization reactions, which vary significantly for different compounds (Yoldas - 1984), makes the order of reactions an important parameter (Jones - 1988) for the polymer structure and the gel homogeneity.

To avoid precipitation and to keep the homogeneity of the gel the options are: previous partial hydrolysis of the alkoxide exhibiting slower reaction rate; complexation of the unstable alkoxide by chelating agents (Jones - 1988); previous copolymerization of two alkoxides (Sakka - 1980).

III.7 - THE MULTILAYER SYSTEM

III.7.1 - THE SELECTION OF REFRACTORY COATING

As discussed previously, it is well-accepted that an oxidation resistant multilayer system, for high temperature carbon materials, should include at least one refractory coating. In the Chapter I, several possible coatings were considered for this purpose but, so far, SiC has been the most successful refractory layer applied on the carbon surface by any technique. SiC coatings have been applied, nowadays, by CVD at very high cost due to the capital equipment involved and the long time to produce a thick layer.

SiC particles have been produced by various chemical routes using sol-gel technique. In each case the objective was to form silicon carbide following the equation (13):

$$SiO_2+3C->SiC+2CO \qquad (13)$$

The system dimethyldiethoxysilane(DEDMS) and tetraethoxysilane(TEOS) (Chen - 1988) produced no gelation for any composition but a 1/1 ratio. The final products were described, by the same author, as a partially amorphous, partially crystalline mixture of SiC, SiO_2 and carbon. Gel production using trifunctional alkoxy and chlorosilanes was investigated using three chemical routes (White[1] - 1987, Fox - 1986). The acid-base route was considered the most versatile and effective method although none of the gels yielded pure SiC upon decomposition. SiC powder was also prepared using methyltrimethoxysilane and phenolic resin in acetone or sucrose in water (Wei - 1984) and the solution was gelled by addition of NH_4OH, at room temperature. In every case, SiC was sintered around 1500°C under flowing argon and the heating rate proved to be the most critical parameter. No SiC could be produced when a heating rate higher than 2°C/min was used.

III.7.2 - THE SELECTION OF GLASSY COATINGS

The ideal glassy coating, to take part in a multilayer system, should exhibit the following properties: i) low permeability to oxygen diffusion, ii) melting point around 500 - 600°C, when the carbon substrate starts to oxidize; iii) inertness to reaction with carbon; iv)

volatilization temperature above the operating temperature and v) coefficient of thermal expansion compatible with the carbon substrate. Many researchers are using B_2O_3 glassy coatings (Chapter I), to fill the cracks of a refractory layer, because its melting point is very convenient, around 450°C. This glass material, however, starts to volatilize around 1200°C (Buckley - 1967) and this is a limitation for any multilayer system aiming to exploit the potential of carbon at high temperatures.

Another choice could be SiO_2 glass, pure or chemically modified by the incorporation of other oxides such as those from alkali metals. Pure SiO_2 exhibits a very low permeability to oxygen diffusion and its CTE value is very close to those of carbon materials. However, it only melts around 1700-1800°C when it really becomes a protective coating. The addition of alkali oxides have been tried with some success, mainly when pack processes are used, but alkali silicates, in general, do not exhibit the same convenient properties described above for pure SiO_2 (Strife - 1988).

The solution must come through the use of multiple glass layers to provide all the necessary requirements. Since 1984 the most complex glasses have been produced using the sol-gel technique and, among them, two prominent glasses are found: SiO_2-TiO_2 and SiO_2-Al_2O_3-LiO_2.

SiO_2-TiO_2 GLASS

Corning Glass Works was possibly the first to produce industrially this glass, in 1971, for the telescope of the Italian Osservatorio Astrofisico Nazionale (Lewis - 1971). For a long time glasses with zero coefficient of thermal expansion had been sought for this purpose and eventually silica glasses containing titania replaced the hard borosilicate and pure fused silica glasses that were used in the past. The values of the coefficient of thermal expansion for SiO_2-TiO_2 glasses, consistently determined by different authors for varied concentrations of titania (Figures 31, 32), approach zero when the titania's concentration is between 6 and 7.40%.

Besides the low coefficient of thermal expansion, SiO_2-TiO_2 glasses also exhibit low permeability to oxygen diffusion and this characteristic is certainly of fundamental importance for a glass in this multilayer system. It is known (Figure 33) that glass compositions with titania below 10% exhibit almost the same oxygen diffusion rate as pure SiO_2, which can be considered excellent.

Although all the valuable qualities cited above are necessary, SiO_2-TiO_2 does not fulfil completely the properties required of an ideal glassy coating, because its melting point (around 1600°C) is too high. In consequence, it will not be able to fill the microcracks, in the SiC layer, before the substrate's oxidation reaction starts. The phase equilibrium diagram (Figure 34) shows that the minimum liquid temperature, for the SiO_2-TiO_2 system, is 1550°C and it is obtained with 10.7% of titania. For carbon materials operating at very high

temperatures, such as 1500-1600°C, this SiO_2-TiO_2 layer can play an important role because it may be soft and impermeable while other glassy layers would be already in a liquid state. Certainly another glassy coating, with lower melting point, to protect the carbon substrate during the heating up process, is necessary.

SiO_2-Al_2O_3-LiO_2

This glass-ceramic has been produced industrially for several applications, including laser equipments (Hiller - 1983), under different names such as Zerodur, produced by Schott, and Cer-Vit, produced by Owens-Illinois. It can also be formulated to exhibit a coefficient of thermal expansion around zero because it partially devitrifies leaving a crystalline phase, ß-eucryptite or ß-spodumene, with a negative thermal expansion coefficient inside a glass matrix (20 or 30% by volume) with a positive one (Roberts - 1982). The CTE value can be adjusted by controlling the volume of ß-eucryptite or ß-spodumene precipitated and for different compositions these values were measured, Table 6, between 0-900°C. The SiO_2-Al_2O_3-LiO_2 glass-ceramic also exhibits a very low permeability to gases in general and its helium permeability of 5.9×10^{-14} cm^3 cm^{-1} s^{-1} bar^{-1}, at 20°C, is even smaller than the value determined for fused silica, 7.1×10^{-6} cm^3 cm^{-1} s^{-1} bar^{-1} (Hiller - 1983).

A proposed liquidus relation for silica-alumina-lithia shows, Figure 35, that it lowest melting temperature, occurs between 1000

and 1050°C when ß-eucryptite crystals are precipitated in the glass matrix.

The properties of this glass-ceramic layer; low CTE, low permeability to oxygen and relatively low melting point, should complete the necessary requirements for a good multilayer system, i.e., a multilayer system able to inhibit the oxidation of carbon materials up to 1500°C during thermocycling conditions. It is necessary to bear in mind that glassy coatings can be tailored for different ranges of operating temperatures, greatly enlarging the flexibility and consequently the applications of this method.

III.8 - GELS PREPARATION

III.8.1 - THE SiC COATING

Dipping or spinning are the common procedures used to apply, industrially, a glassy coating on glasses and, in this case, sols but not gels are used. The thickness of these glassy layers are, therefore, strongly limited up to 0.7 um even after several dipping or spinning operations (Sakka - 1987, Scriven - 1988).

It is known that a refractory coating on the carbon surface has two objectives: the first is obviously to act as a barrier for oxygen diffusion, inhibiting the oxidation. The second objective is to avoid carbon diffusion outwards because it reduces the SiO_2, from the glassy layers or resulting from the oxidation of an external SiC layer,

producing silicon monoxide which is volatile around 1500°C (Strife - 1988). If a successfull SiC coating is to be applied on a carbon surface it cannot be subjected to thickness restrictions imposed by the dipping or spinning techniques.

It was decided to make an attempt to generate SiC from the gel state, varying as many parameters as convenient, to produce a coating which was as thick, as uniform, and as free of cracks as possible. The parameters chosen to be varied were the amount of water, the type of solvent, the type of catalyst and the use of an additive, e.g., glycerol.

The amount of water has a strong effect on the hydrolysis rate and consequently on the chain size and cross-links occurring during the polymerization step. Theoretically one would accept that larger amounts of water would lead to the formation of polymeric chains, more suitable for coatings, but Butts (Butts - 1988) showed that a moderate amount of water can produce a better wettability of the substrate and, therefore, this parameter should be investigated. The solvent has a strong influence in the drying and the gelling process and, although it is known that low vapour pressure solvents normally produce less cracks on coatings their influence on wettability and coating thickness is not well defined. The most well accepted catalyst, for this application, is usually an acid. Bases are normally used for particle production but few experiments using base catalysts were performed in this study. Glycerol was used, as a drying additive, to increase the drying time and favour a uniform pore size distribution that, in theory, should provide a coating with fewer cracks.

Ten gels were prepared with four, eight and sixteen moles of water per mol of TEOS, using ethanol and propanol as solvent, with and without glycerol as listed below.

MOLAR COMPOSITION OF THE ACID-CATALYSED GELS

gel number	H_2O/TEOS	solvent	glycerol
32	4	ethanol	no
44	4	propanol	no
52	8	ethanol	yes
56	8	ethanol	no
65	8	propanol	yes
68	8	propanol	no
77	16	ethanol	yes
80	16	ethanol	no
89	16	propanol	yes
92	16	propanol	no

A stoichiometric amount of phenolic resin BP cellobond J2027L, solubilized in acetone, was used as an external carbon source for the SiC reaction, assuming 50% of carbon yield (Wei - 1984); 70 cm^3 of acetone was used to dilute each 23.5g of phenolic resin. Hydrochloric acid was used, as catalyst, in a fixed amount of 0.01 mol/mol of TEOS. Both solvents, i.e, ethanol and propanol were kept at a constant ratio of 4 mol/mol of TEOS and when glycerol was used its amount was also constant and equal to 1 mol/mol of TEOS.

The gels were prepared by solubilizing TEOS with the solvent, during five minutes under constant agitation with magnetic stirrer under reflux, in a closed vessel. The catalyst was mixed with the corresponding amount of water and this mixture added dropwise, using an addition funnel, to the TEOS solution. The mixture was heated up to 70°C for 2 hours during hydrolysis. Afterwards, the phenolic resin solution was added using the same dropwise procedure

and the temperature was maintained for one more hour. When glycerol was used it was added to TEOS immediately after the solvent and before the water. The sols obtained by the procedure describe above, after having the pH recorded (Table 7), were left to gel in an oven at 60°C. The gelling process was stopped just at the beginning, i.e., when the mixture was able to keep the vase shape.

Attempts were made to produce a homogeneous gel, suitable for coatings, using ammonium hydroxide as catalyst and the same phenolic resin as carbon source, but no successful result was achieved. The gels, when homogeneous, exhibited a powdery appearance which was not suitable for this application. In every case the concentration of the solvent was 4 mol/mol of TEOS and the compositions produced and the appearance of the gels are presented in Table 8.

III.8.2 - THE SiO_2-TiO_2 COATING

TEOS has been the most frequently-used Si source to produce a SiO_2-TiO_2 glass while the titanium source has usually been selected from titanium ethoxide (Yoldas - 1980), titanium tetra isopropoxide (Kamiya - 1974, Gonzalez-Oliver - 1982, Lirong - 1986,1988, Cheng - 1988, Deng - 1988), titanium butoxide (Beir - 1986), polytitanosiloxanes (Gunji - 1989) and titanium chelate (Abe - 1988).

The major problem to be considered during this gel production is the maintenance of a homogeneous solution because strong differences in the hydrolysis rate for the Si and Ti alkoxides are observed and they can lead to high precipitation of titanium compounds that hydrolyse

faster. To avoid this problem, most of the authors preferred to hydrolyse initially the Si alkoxide, with the minimum amount of water, followed by the addition of the titanium alkoxide and the necessary amount of water to complete the desired composition (Yoldas - 1980, Cheng - 1988).

After that a homogeneous gel is produced the crystalization of titania (rutile or anatase) should be avoided if the properties of the glass are to be achieved. Most of the works published about this gel are dedicated to this subject and it is well accepted that concentrations of titania lower than 10% will produce an amorphous glass even at temperatures higher than 1000°C (Kamiya - 1974). Gels with a higher concentration of titania, 25%, where produced by Yoldas (Yoldas - 1980) without crystallinity, even when fired up to 1200°C. The firing procedure and not only the relative amount of titania has influence on the glass crystallization. Successful bulk pieces were produced, in most of the cases, at a slow heating rate with several steps (Gonzalez-Oliver - 1982, Lirong - 1986,1988, Abe - 1988, Beir - 1986) up to 1000°C. The only exception found in the literature was the work presented by Deng (Deng - 1988) where the best results were achieved at very high heating rates (20-50°C/min) with plateaus at 1200-1250°C and 1450-1500°C. The same author observed the formation of anatase crystals around 1250°C and their disappeareance at 1450°C, due to their dissolution as a result of the high mobility of the Ti ions, leading to the production of amorphous bulk pieces of glass. The gel preparation is also related to glass crystallization; development of high amounts of Ti-O-Ti bonds, identified by X-Ray diffraction or IR, in the gels leads to the formation of rutile and anatase crystals (Gunji - 1989, Cheng - 1988), around 900°C.

Considering the works described above, it was decide to prepare a SiO_2-TiO_2 gel using titanium tetra isopropoxide and TEOS, as Ti and Si sources respectively. Initially ethanol was used as the solvent for the alkoxides but, after the analysis of the results achieved for the SiC coating, the solvent was changed to acetone. The objective consisted in producing a gel that could be soft enough to be applicable by brushing, i.e. where the gelation and the ageing process were not fully completed, and able to leave a glassy layer, after firing, with a concentration of TiO_2 between 6 and 10%. In fact, to be very conservative, the optimum Ti concentration range should be 6-7.5% to provide a TiO_2 layer with CTE value near zero, low permeability to oxygen diffusion and melting point around 1600 ^oC. The amount of water used was always around twice the stoichoimetric amount required for complete hydrolysis of the alkoxides, 9.4 mol H_2O/mol TEOS due to the results observed for the SiC coating, while the HCl concentration was kept constant, 0.01mol/mol TEOS. The molar gel compositions produced and the theoretical SiO_2-TiO_2 relative weight percentages are listed below:

gel number	**acetone/TEOS** molar ratio	**SiO_2/TiO_2** %
1	6.4	81.3/18.7
2	9.0	81.3/18.7
3	9.0	88.2/11.8
4	9.0	85.0/15.0
5	9.0	83.0/17.0
6	9.0	92.5/7.5
7	9.0	90.5/9.5

Ti[iso] - titanium tetra isopropoxide

These gels were prepared diluting TEOS in acetone and stirring for 5 minutes. Just one mol of water, with the total amount of acid, was added dropwise and left to promote the TEOS hydrolysis during 1 hour around 67°C. Afterwards the mixture was left to cool to room temperature when titanium tetra isopropoxide was added dropwise, under argon atmosphere, and stirred for more than 1 hour. The amount of water necessary to complete the formulation was then added dropwise and the mixture was allowed to gel inside an oven at 60°C until it was able to keep the vase shape.

III.8.3 - THE SiO_2-Al_2O_3-LiO_2 COATING

Two important points were identified when this glass-ceramic material was selected. The first was related to the choice of the precursors and the second with the precipitation of an adequate amount of ß-eucryptite crystals to leave a coating with very low permeability to oxygen, low CTE value and melting point around 1000°C. The adequate amount of ß-eucryptite crystals is dependent on the composition of the mixture and its firing procedure.

TEOS is still the most usual source of Si while the Al and Li sources varied widely among the published research works. The possible Al sources include inorganic and organic compounds such as $AlCl_3.6H_2O$ (Coury - 1987, Lambilly - 1988), $Al(NO_3)_3.9H_2O$ (Anderson - 1987, Coury - 1987, Lambilly - 1988), aluminium sec butoxide and aluminium propoxide (Coury - 1987, Lambilly - 1988). It was decided to restrict the choice to alkoxides because they can produce better coatings on SiC than the inorganic compounds (Coury -

1987). Between the alkoxides, the aluminium sec butoxide was preferred because aluminium propoxide exhibits low solubility in most of the solvents used, such as alcohols (Coury - 1987). Among the possible Li sources, lithium methoxide was demonstrated to be the best organic precursor, while lithium nitrate is accepted as the best inorganic precursor (Wallace - 1984, Anderson - 1987) and these compounds have been systematically used to produce this glass-ceramic (Schwartz - 1986, Orcel[1] - 1986). As no further technical information is available on the use of these precursors, lithium methoxide was selected for this work to keep the alkoxide line in the gel production.

The range of compositions produced for this glass-ceramic material is very wide and only those linked with properties relevant to this work (Takeda - 1974, Corning Glass Works -1971) were considered. Twenty different glass-ceramic compositions of SiO_2-Al_2O_3-LiO_2 and their coefficients of thermal expansion (Corning Glass Works - 1971) are listed in Table 6 and from this list the following three compositions were selected due to their low CTE values and low melting points (Figure - 36).

sample	SiO_2	Al_2O_3	LiO_2	CTE($/^oC$ x10^7)
	%	%	%	
W1	60.0	16.0	24.5	1.3
W2	75.0	10.0	15.0	-1.2
W3	60.0	21.7	18.3	1.6

The formation of the crystalline ß-spodumene phase, between 375-400°C, was identified (Orcel - 1986) using 66.7%wt SiO_2 - 22.6%wt Al_2O_3 - 7.6%wt TiO_2 - 3.1%wt Li_2O while ß-eucryptite crystals with

some impurities of ß-spodumene were achieved (Covino - 1986) by heating a composition with 61.35%wt SiO_2 - 27.97%wt Al_2O_3 - 4.08%wt Li_2O - 2.30%wt TiO_2 (and other minor components) at 2.93°C/min up to the nucleation temperature (735°C) and holding it during 6 hours; heating again at 2.17°C/min up to the crystallization temperature (800°C) and holding it during 96 hours and finally cooling at 8°C/min. A composition with 15mol% of lithium was crystallized above 600°C and nucleated around 700°C (Schwartz - 1986), showing that a larger amount of lithium did not change considerably the main temperature parameters, i.e. the crystallization and nucleation temperatures.

TEOS, aluminium sec-butoxide and lithium methoxide were selected to be the sources for Si, Al and Li, respectively, as it was noted previously. Ethanol was initially used as the solvent for TEOS but was replaced by acetone after noting the results achieved for the SiC coating. A composition that will permit the formation of ß-eucryptite crystals and, in consequence, produce a coating with low CTE value and melting point around 1000°C should comprise: SiO_2 - 60%, Al_2O_3 - 16%, LiO_2 - 24%. This composition is located on the phase diagram (Figure - 36), together with those produced by Corning (Corning Glass Works - 1971) to facilitate the identification of its expected CTE value, $1.3\text{-}1.6\times10^{-7}$/°C, and melting point (1000°C). This selected layer will keep its low melting point and CTE value even if minor changes occur in its composition during the firing procedure, as shown in Figure 36.

The molar composition of this gel was maintained in all the attempts to produce a material soft enough to be brushed on the carbon

surface with exception of the solvent, which was varied between 8 and 76.4 mol of acetone/mol of TEOS:

TEOS : Al[sec] : Li[met] : water : HCl

1	0.315	0.619	11	0.01

Al[sec] - aluminium sec-butoxide
Li[met] - lithium methoxide

TEOS was solubilized in analar acetone and stirred for 5 minutes. The total amount of catalyst was added and the alkoxide left to hydrolyse, using the water content in the solvent, for 3 hours at 70°C. The mixture was left to cool to room temperature when aluminium sec-butoxide was added and stirred during 30 minutes. Afterwards the total amount of lithium methoxide was added and the mixture was stirred again for 30 minutes. The solution was heated up to around 57°C, for 1.5 hours, to solubilize the last alkoxide, i.e. lithium methoxide. The amount of water necessary to complete the formulation was added dropwise to the solution, at room temperature, and the sol was left to gel at this same condition.

CHAPTER IV

RESULTS

The major part of the results obtained in this work are presented in this chapter (the preparation of the gels was described in Section III.8). The chapter begins with an account of the characterization of the gels used to produce the primary SiC coating (Section IV.1). The performance of the SiC coating on two types of carbon substrate: a fine-grained engineering graphite and a carbon-carbon composite is described in Section IV.2. The final section of the chapter deals with the development and application of the two glassy coatings: SiO_2-TiO_2 and SiO_2-Al_2O_3-LiO_2 to the carbon substrates.

IV.1 - SiC COATING - CHARACTERIZATION AND GEL SELECTION

IV.1.1 - INTRODUCTION

To characterize and select the most convenient gel, from the ten described in the Chapter III, an inexpensive carbon material (electrode graphite) was used as substrate. The techniques involved in this characterization and selection were: **Scanning Electron Microscopy (SEM)** - to visualize the shrinkage of the gels on the carbon surface and the coating appearance before firing, **Fourier Transform-Infra-Red (FT-IR)** - to follow the gelation process and to identify SiC formation, **X-Ray diffraction analysis** - to confirm formation of SiC, **X-Ray Dispersive Analysis (EDX)** - to locate Si on the carbon

surface and assess the coating quality and **Thermogravimetric Analysis (TGA)** - to determine the oxidation resistance afforded by the coating.

The electrode graphite samples (diameter - 45mm, thickness - 20mm) and were polished with 500 grade emery paper, cleaned in an ultrasonic bath with Genklene and dried. The coating procedure for the carbon samples always followed the same sequence: a layer of the gel was brushed on the carbon surface and left to dry (in air for 48 hours and at 60°C for 4 hours); two others layers were applied with the same drying procedure. The coated carbon samples were fired at 2°C/min up to 1450°C, with a soaking time of 4 hours in an argon flow of 600cm^3/min, to promote the SiC formation. This procedure was repeated several times to obtain the convenient SiC layer thickness.

IV.1.2 - SCANNING ELECTRON MICROSCOPY (SEM)

After the gels were dried and before the firing procedure, the surface of the samples were observed in the electron microscope Jeol-JSM-T330, without any special preparation except for a coating of gold applied by sputtering during 3min to increase electrical conductivity of the surface. As expected, all the gels exhibited shrinkage leading to a mosaic layer structure. The effects of the water/alkoxide ratio, the solvent - ethanol or propanol and glycerol (DCCA) were evaluated by monitoring crack widths, the grain size of the mosaic structure, the internal porosity and the flatness of the particles.

WITHOUT GLYCEROL (DCCA)

Increasing the water/alkoxide ratio produced a finer mosaic structure layer for both solvents used, (ethanol and propanol), after the drying process (Figures 37, 38, 39 and 40). Inside of an area of 78.7mm x 48 mm, approximately 5 particles of the mosaic structure were found for the gels produced with 8mol water/mol alkoxide, for both solvents (ethanol and propanol), and 25 and 15 particles when the water/alkoxide ratio was increased to 16 mol water/mol alkoxide for ethanol and propanol, respectively. Increasing the water/alkoxide ratio, also produced an increase in the mosaic particles' internal porosity of the dried gels 56 and 80 (Figures 37B and 38B), produced with ethanol and with 8 and 16 mol water/mol TEOS, from a maximum diameter of 3.3 mm to 7.3 mm. On the other hand, the same variation in the water/alkoxide ratio for the gels 68 and 92 (Figures 39B and 40B), using propanol as the solvent, produced no change in the mosaic particles' internal porosity.

WITH GLYCEROL (DCCA)

The increase of the water/alkoxide ratio did not produce any change in the mosaic structure for both solvents, ethanol and propanol (Figures 41, 42, 43 and 44 - respectively for the gels 52, 77, 65, 89). The mosaic particles' internal pore size was reduced and its distribution was found to be more uniform when the first solvent, i.e. ethanol, was used (Figures 41B and 42B). When the second solvent, i.e. propanol, was used no internal porosity was observed in the mosaic particles and even the few and narrow cracks observed with 8 mol water/mol

alkoxide disappeared completely when this parameter was increased to 16 mol water/mol alkoxide (Figures 43B and 44B).

The surface of the gels, before being fired, were tilted and photographed at 65^{o} and three typical behaviours were observed. All the mosaic layers exhibiting large internal particle porosity were almost flat (Figure 45) while those with a very narrow pore distribution were slightly bent out of the carbon substrate (Figure 46). The extreme case was observed for the mosaic layers where no internal porosity could be observed and, in this case, the particles were very well bent out of the surface exhibiting an "U" shape (Figure 47).

IV.1.3 - FOURIER TRANSFORM INFRA-RED (FT-IR)

Before being fired, all the gels brushed on the surface of electrode graphite samples were analysed using the dispersive reflectance technique of the FT-IR Perkin-Elmer model 1720 without any special sample preparation. The technique was found to be very useful because the sensitivity was enough to follow not only any variation of the gel composition, but also the gelation process. An uncoated electrode graphite sample was always used as background and in every case 20 scans were run with a resolution of $2cm^{-1}$. The main peaks observed in these spectra for both dried (in an oven $60^{o}C$ during 24 hours) and wet gels can be assigned as showed in table 9 (Orcel - 1986).

The relationship between the peaks **e** and **f** and the shape of broad region **a** for the spectra of the dried gels 56 and 52 (Figure 48) and gels 68 and 65 (Figure 49) can be used to estimate qualitatively the variation of the extent of gelation when glycerol is introduced in the mixture. The peaks **e** and **f** can also be used to compare the intensity of the gelation during the drying process when spectra for the same gels are analysed before and after drying. For example figures 50 and 51 show, respectively, the spectra for the wet and dried gels 56 and 52. The dried gels produced with glycerol consistently exhibited larger absorbance differences between peaks **e** and **f** for both solvents used (Table 10), i.e. ethanol and propanol (Figures 48 and 50). Furthermore, they did not show the same large difference in the absorbance of these peaks, before and after drying (Figure 51), as was shown by the gels produced without the additive (Figure 50) (Table 11).

When the samples coated with the dried gel were fired at 1450^{o}C, following the procedure already described, a SiC coating was identified by FT-IR on the surface of the carbon substrate for eight gels. When the samples were fired twice all the gels exhibited a detectable amount of SiC. The spectrum produced by gel 56 (Figure 52), for example, can be compared with another one produced by an industrial SiC powder using FT-IR diffusive reflectance technique. The typical SiC peak can be clearly identified in both spectra but the formation of SiC on the carbon surface was further confirmed by X-Ray diffraction analysis.

IV.1.4 - X-RAY DIFFRACTION ANALYSIS

A PW 1730/10 X-ray generator, a PW 22/73 long fine focus 2kW copper target X-ray tube (40kV, 20 mA) and PW 1820/00 computer controlled vertical diffractometer goniometer was used for this analysis. The spectrum produced, using program 155, by the graphite substrate alone and the same substrate coated with the fired sol-gel coating (Figure 53) show, conclusively, that SiC was produced on the surface of the sample. However, to further characterize the formation of a SiC coating and to assess its quality, energy dispersive X-Ray analysis (EDX) was used. Table 12 shows the standard and obtained X-Ray diffraction peaks for graphite and SiC.

IV.1.5 - X-RAY DISPERSIVE ANALYSIS (EDX)

The coatings produced by each gel were analysed and mapped for Si using the Scanning Electron Microscope Jeol 35C and EDX. A typical result for gel 56 is presented at two different magnifications (Figure 54) for samples fired once, twice and three times. A continuous SiC coating was achieved, in this particular case, when the sample was fired three times. Different extents of homogeneity in the SiC layer were produced when gels of different chemical compositions were used; some of them are compared, as examples in Figures 55 and 56, using the coating generated by gel 56 as standard. While the SiC coating generated from gel 56 is continuous and uniform, with a thickness between 10 and 20 μm, the coating produced using gel 80 (Figure 55) is discontinuous. On the other hand, the coatings produced using gels 89, 77 (Figure 55) and gel 92 (Figure 56) are continuous but their thicknesses are not uniform. In every case and for any gel used,

however, the deep penetration of Si inside the open porosity of the substrate (more than 100 μm) should be emphasised.

IV.1.6 - THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis is the most important and decisive experiment to assess the coating quality, because it is directly related to the oxidation protection that will be confered to the substrate. Using TGA was possible to measure not only the protective effect of each individual gel, but also the behaviour of the coating when several firings were made. These experiments were conducted in a Stanton-Redcroft 750 thermogravimetric balance where the samples were oxidised under flowing air, at a constant flow rate of 50 cm^3/min. The isothermal temperature used to measure the weight loss was 920°C and it was achieved using a heating rate of 100°C/min. After this initial gel selection, the TG tests were performed using a thermobalance Setaram DTA92.

- The effect of the number of firing times

EDX analysis showed that the repetition of the firing procedure (IV.1.1) produced a thicker and more continuous coating, although it does not necessarily imply an increase in oxidation protection. The weight loss of electrode graphite samples coated and fired once, twice and three times were compared with the weight loss exhibited by an uncoated sample to determine the effect of the number of firings on the

oxidation protection. Without exception for all the ten gels analysed, the highest oxidation protection was achieved when the sample was fired just once and typical examples are shown in figures 57 and 58 and compared in table 13. On the other hand, a consistent pattern was not observed when the weight losses between the samples fired twice and three times were compared. In this case the gels prepared with 8 mol water/mol TEOS, using both solvents and with or without glycerol, (gels 52, 56, 65 and 68) and the gel prepared with 16 mol water/mol TEOS, using ethanol and no additive, (gel 80) exhibited better oxidation protection when they were fired three times than when they were fired twice (Figure 58). All the other gels showed the opposite behaviour, i.e. better oxidation protection for two firings than for three firings, e.g. gel 44 (Figure 57). A sample with a single SiC layer, i.e. brushed just once but fired twice exhibited the same weight loss as an uncoated sample (Figure 59).

- The effect of the chemical parameters

- water/alkoxide ratio

The thermogravimetric analysis of the samples fired once (Figure 60), fired twice (Figure 61) and three times (Figure 62) showed that among the three samples exhibiting highest oxidation protection, in each case, were always those coated with the gels prepared with 8 mol water/mol TEOS (gels 56 and 68). The third sample to complete each set changed depending on the number of firings from the one coated with the gel 65, also prepared using 8 mol water/mol alkoxide, to the sample coated with the gel 32 (4 mol water/mol TEOS) and gel 80 (16 mol water/mol TEOS). These results emphasise the

predominance of the gels prepared with 8 mol water/mol TEOS over all the others in affording oxidation protection to the graphite substrate. It was verified in some experiments that samples coated with inadequate chemical composition exhibited worse TG results than uncoated samples what can be explained by damages caused to the microstructure of the substrate, due to thermocycling, and not compensate by the gel performance.

- solvent and additive

The thermogravimetric analysis for the samples fired once (Figure 60), fired twice (Figure 61) and three times (Figure 62) also show that the best oxidation protection was achieved with gels prepared without glycerol (gel 56, gel 68, gel 80 and gel 32) as DCCA. However a clear distinction of the best solvent to be used in future developments was not found since the improvements in the oxidation resistance provided by gels 56 (using ethanol) and 68 (using propanol) were very close to each other. Therefore it was decided that more experiments should be done to improve the understanding of the effect of the solvent in the coating production.

IV.2 - PRIMARY SiC COATING

IV.2.1 - THE GEL ENHANCEMENT

With the support of the results described in the previous section, gel 56 (8 mol water/mol alkoxide and no glycerol) was selected for

further investigations on the effect of the solvent on the oxidation resistance afforded by the SiC coating.

All the ten gels prepared initially used ethanol or propanol to solubilize the alkoxide (TEOS) and acetone to solubilize the phenolic resin. To emphasise the effect of the solvent on the formation of the SiC coating the chemical composition of the mixture was changed in order to observe the results for two extreme cases, i.e. a gel prepare only with ethanol and another prepared only with acetone to solubilize both the TEOS and the phenolic resin. Therefore two more gels were prepared as shown below:

a) Gel **8Eth** : This gel was prepared using only ethanol to solubilize both the alkoxide and the phenolic resin (carbon source). The volume of ethanol used in this gel was the same as used in gel 56.

Molar composition of gel 8Eth

TEOS	ETHANOL	WATER	HCl
1	4	8	0.01

b) Gel **8Ac** : This gel was prepared using only acetone to solubilize both the TEOS and the phenolic resin and its volume was the same as used in gel 56.

Molar composition of gel 8Ac

TEOS	ACETONE	WATER	HCl
1	3.2	8	0.01

FT-IR spectra from the dried gels 8Ac, 56 and 8Eth on graphite were produced on graphite to compare the polymerization rate of these three gels. There is not a considerable variation between the relative intensity of the peaks **e** and **f** (Figure 63), however, the peak **g**, around 450 cm^{-1},assigned to the rocking Si-O-Si movement (Orcel - 1986), is stronger when one changes from the gel with ethanol (8Eth) to the gel with acetone (8Ac). Peak **g**, is slightly shifted towards a smaller wavenumber in the spectrum of the gel 8Ac than in the gel 56.

The gels 8Ac, 8Eth and 56 were fired five times on POCO graphite samples (5mmx10mmx2mm) to assess the coating uniformity. Eight different areas were analysed in each sample at high magnification (X3000) and four of them are shown, as an example, in figures 64 (gels 56 and 8Eth) and 67 (gel 8Ac). The gel 8Ac produced the more uniform coating which is free-of-cracks and with a thickness around 10 μm.

A comparative thermogravimetric analysis for two samples coated with each one of these gels (8Ac, 8Eth and 56), figure 66, shows that the gel 8Ac provides higher protection to the carbon substrate than any other, while the gel 8Eth exhibited results similar to the uncoated substrate. With these results the gel to produce SiC coatings

was considered optimized and the gel 8Ac was therefore selected to take part in the multilayer coating system.

IV.2.2 - CHARACTERIZATION ON ENGINEERING GRAPHITE GRADE AND C/C COMPOSITE SURFACES

The selection of the best gel to produce SiC coatings on carbon surface enabled this project to proceed to a second stage, that is the development of a protective multilayer system to the carbon substrate. One engineering graphite grade, ZXF 5Q Poco graphite, and a C/C composite densified only by impregnation, KKarb C/C composite, were used as substrates. ZXF - 5Q is an extremely fine-grained graphite with a filler size smaller than 1μm. The KKarb C/C composite is a 2-D woven carbon-carbon composite with X-rayon carbon fibre tows in a 5-harness satin weave and a resin/pitch carbon matrix.

Poco graphite and KKarb C/C composite samples were coated and fired five times with the gel 8Ac and analysed by EDX (Figures 67 and 68). A comparative analysis of the EDX image for Si on Poco graphite and KKarb C/C composite shows that a thicker SiC coating (about 20 μm) was obtained on the surface of the graphite than on the surface of the C/C composite (about 7 μm). The same figures also show that due to the almost complete absence of open porosity in Poco graphite (SEI - Figure 67) little infiltration of Si could be observed in this material. On the other hand, the large and high number of cracks observed on the surface of the C/C composite (SEI - Figure 68) permitted a very deep (more than 150 μm) and large penetration of

silicon. An optical micrograph of the SiC coating (around 30 μm thick), on the internal surface of the suspension hole of a Poco graphite sample, shows the quality of the interface between this material and the substrate (Figure 69).

IV.2.3 - THERMOGRAVIMETRIC ANALYSIS

The Poco graphite and KKarb C/C composite samples were polished with 500 grade emery paper, washed with genklene and dried.

Before the Poco graphite and the KKarb C/C composite samples were coated with the gels, a few samples were heat treated up to 1500°C in helium using a heating rate of 99.99°C/min using a Setaram DTA 92 thermobalance. This was done to determine if volatiles were present that could damage the coating. A repetitive weight loss was observed, in helium, for the graphite samples but not for the C/C composite samples. It was, therefore, decided to submit all of the C/C composite samples to a heat treatment up to 1450°C, with a soaking time of 20 hours before the SiC layers were applied. The TGA curves of a Poco graphite and a heat-treated C/C composite sample, submitted to 1500°C during 15 min (Figure 70), show 1% and 0.3% weight loss, respectively and these values were considered satisfactory for the coating application.

It was decided to evaluated the performance of the SiC coating up to 1200°C, instead of higher temperatures, due to the limited

protection provided by the coatings at this stage. Poco graphite samples coated with the gel 8Ac and fired up to five times were oxidised in the thermobalance Setaram DTA 92, at 99.99°C/min using an air flow of 1.5 l/h. The weight losses determined for the coated samples are compared with the weight loss exhibited by an uncoated sample in figure 71. Both the weight loss and the DTG were systematically reduced with the increase of the number of firings. An unexpected large depression (Figure 71) was observed in the DTG curve of the uncoated sample, starting around 950°C and reaching its minimum around 1100°C. This event was also observed for the samples coated with SiC and fired once and three times but not for the samples fired five times. For the coated samples, the depression was reduced and its onset was delayed to temperatures around 1100°C.

The SiC coatings applied on the KKarb C/C composite surface, even when fired 5 times, did not show the same benefit on oxidation resistance (Figure 72) as found for Poco graphite. With this substrate (C/C composite) a depression was again observed for the DTG signal (for the uncoated sample) but it was smaller than the depression observed for the uncoated Poco graphite sample and it commenced only around 1100°C instead of 950°C. Once more this depression was reduced when the C/C composite was coated five times with SiC. The TG and DTG curves (Figure 72) show that the oxidation reaction started around 550°C for the coated C/C composite sample (SiC fired five times) while for the unprotected sample it started around 480°C. The DTG curves also indicate (Figure 72) that there is not a large difference between the oxidation rates for the uncoated sample and the sample coated with SiC.

IV.3 - SiO_2-TiO_2 COATING

IV.3.1 - CHARACTERIZATION

It was shown (Chapter III) that the desired composition of the SiO_2-TiO_2 glassy layer should comprises 6 to 7.5 %wt of TiO_2. The gels 2, 3, 6 and 7 (section III.8.2), selected among the seven prepared, were fired on a SiC layer previously applied to Poco graphite to determine the most adequate firing procedure and the variation of the original chemical composition during firing. The firing procedures used and the variations observed in the original chemical compositions are summarised in Tables 14 and 15, respectively. The chemical compositions of the glassy layer were determined directly on the surface of the samples by EDX using the Zaf 4 program and standards of Columbo, 100% pure Si and 100% pure Ti (Jeol 35C) to determine the relative percentages of Si and Ti that were converted and presented in Table 15 in terms of SiO_2 and TiO_2. The percentual change in the chemical composition of the SiO_2-TiO_2 coating was determined by the absolute value of the difference in TiO_2, before and after firing, divided by the amount of TiO_2 existing in the coating before firing.

The firing procedure number 1 reduced strongly the relative amount of Si in the composition of the gel number 2 and produced at the same time a reasonable amount of undesirable TiC in this glassy layer (Figure 73 and Table 16). When the gel number 2 was fired using the procedure number 2, i.e. fired in air up to 400°C and in Ar up to 1450°C, the substrate was partially oxidised and in consequence it was

decided to lower the firing temperature in air to 300°C. The firing procedure number 3 was therefore carried out and the attack on the substrate, measure by weight change, was avoided. Firing procedure number 3 also avoided the formation of TiC and it was therefore adopted to sinter this glassy layer. TiC is considered an undesirable material in this protective coating because it oxidises faster than SiC (Naslain - 1981 and Rossignol - 1982) and does not exhibit any beneficial property for this multilayer system. TiC was probably formed by carbothermic reduction of TiO_2 (equation 14) where the carbon source should be primarily the residual carbon from organic compounds trapped inside the coating at temperatures around 1005°C and 1155°C (Stull - 1971). The use of an oxidising atmosphere at low temperatures (up to 300°C) burned out the residual carbon without oxidising the substrate.

$$TiO_2 + 3C \text{ ---> } TiC + 2CO \qquad (14)$$

The summary of the chemical compositions, presented in table 15 shows that the gel 6 exhibits, after firing, exhibits the closest chemical composition to the desired one, i.e. 6-7.5 %wt of Ti, and in consequence it was selected to take part in the multilayer system.

Once five firings of this coating (SiO_2-TiO_2) were produced, the samples were heated treated up to 1600°C (15°C/min with a soaking time of 15 min), in a Astro furnace, to melt the glassy layer. TGA and EDX were performed with both as-fired and as-fired plus heat treated coatings to assess the coating quality and determine the effect of this heat treatment on the oxidation resistance.

IV.3.2 - SCANNING ELECTRON MICROSCOPY AND X-RAY DISPERSIVE ANALYSIS

EDX images for Si and Ti (before heat treatment up to 1600°C) on Poco graphite and KKarb C/C composites (Figures 74 and 75 respectively) show that a Si-containing continuous layer forms on the surface and it was found inside of the porosity of both materials, with a penetration of 150 μm deep inside the C/C composite crack. However, the Ti layer does not seem to exhibit the same continuity on the C/C composite surface as on the graphite surface and it was not found inside the graphite porosity at all. EDX images for Si and Ti (before heat treatment up to 1600°C) inside of a C/C composite pore (Figure 76) show that while Si penetrated deeply the crack system. Ti was just identified at the entrance of cracks. EDX images for Si and Ti (after heat treatment up to 1600°C), figure 77, show that Ti could be found more than 100 μm deep inside the pore and the same figure also suggests that this large pore was blocked (SEI - Figure 77), around 40 μm deep, by the SiO_2-TiO_2 glass.

A 65° microphotograph of the top side of a C/C composite sample (Figure 78) coated with SiC and SiO_2-TiO_2 glass, heat treated up to 1600°C, shows a very smooth surface around two defects: the first, magnified in figure 79, suggests that part of the coating was blown up opening a hole and the second is a crack around 150 μm long. The lateral side of this same C/C composite sample, where the original pattern of the composite can still be observed underneath the coatings, shows some cracks in the middle of the fibers bundles (Figures 80 and 81) about the same size of the one described above. It is also possible to

identify in these figures, specially in figure 80, that there are also cracks on the glassy coating running along the fiber-matrix interfaces.

IV.3.3 - THERMOGRAVIMETRIC ANALYSIS

A beneficial effect of SiO_2-TiO_2 coating applied on SiC for KKarb C/C composite was observed on the thermogravimetric and DTG curves, during oxidation in flowing air (1.5 l/h) using a heating rate of 100°C/min up to 1200°C, when the sintered SiO_2-TiO_2 glassy layer was heat treated up to 1600°C (Figure 82). In this case the beginning of the oxidation reaction was delayed up to 650°C (Figure 82 - DTG curves) and a significant improvement on the oxidation resistance of the C/C composite sample found at higher temperatures.

The same oxidation tests were repeated for the Poco graphite samples using the same oxidation procedure already described (Figure 83). The TGA results for the samples coated with this glassy layer (SiO_2-TiO_2 on SiC) without the heat treatment up to 1600°C were worse than those exhibited by samples coated only with SiC. When the SiO_2-TiO_2 layer was heat treated up to 1600°C, the DTG curves (Figure 83) show that both coated samples, i.e. coated with SiC and with SiC plus SiO_2-TiO_2, exhibited the same behaviour until around 1100°C, however, above this temperature the DTG curve for the sample coated with the glassy layer approached the curve of the uncoated sample.

IV.4 - SiO_2 - Al_2O_3 - LiO_2 COATING

IV.4.1 - CHARACTERIZATION

The positive characterization of this silicate coating should be done on a carbon material to assess the variations in its chemical composition due to possible carbothermic reduction of the oxides. It is also important that this characterization should be also done as a coating, not as a bulk piece, because the stability and the incorporation of alkalis into silicates are still a problem to be overcome (Schwartz - 1986). These particular features, associated with the fact that Li cannot be identified by X-Ray dispersive analysis (it is a very light element), did not permit a positive identification of the silicate formed after firing with the techniques used in this project. X-Ray diffraction analysis is the most usual and efficient way of identifying this glass-ceramic material however the main X-Ray peaks of a large number of lithium-aluminium-silicates are close to the graphite peaks (Table 17). The resolution of the spectrum is sufficient to avoid the lithium-aluminium-silicate peaks show themselves up like shoulders of the massive peaks and broad regions of the graphite substrate. The X-Ray diffraction analysis of this coating on SiC (Figure 84) shows two small peaks that appear as shoulders of the main carbon peak. The formation of eucryptite became one of the possible phases formed during firing; however, another lithium-aluminium-silicate, e.g. $Li_2Al_2Si_2O_8$, can also be present. The main difference between these two silicates is a third peak in intensity which did not show itself up because of the small concentration of SiO_2-Al_2O_3-LiO_2 in the coating, compared with carbon substrate, and because it will produce another

very small shoulder on the main carbon peak or the main SiC peak, respectively.

The analysis of this glass-ceramic coating in the SEM (Figure 85) shows a vitreous appearance exhibiting several hair-line cracks, less than 0.5 μm wide and as long as 500 μm, running randomly on its surface. The C/C composite pattern could not be identified in this case because the coating blocked completely any visual access to the substrate underneath, even on the lateral sides of the sample where the thickness is usually smaller than on the top side. These hair-line cracks produced on this glass-ceramic coating cannot be related with the original defects of the substrate as it was suggested when the results of the SiO_2-TiO_2 coating were presented.

EDX for Al (Figure 86) shows that the penetration of this glass-ceramic material inside the C/C composite porosity was more uniform and deeper than the penetration observed for the SiO_2-TiO_2 glass. In fact where Si was found inside of the sample, Al was also also found, indicating that the penetration achieved for the gel that produced SiC was the same or almost the same as that achieved for the SiO_2-Al_2O_3-LiO_2 gel.

IV.4.2 - THERMOGRAVIMETRIC ANALYSIS

A comparative DTG analysis (Figure 87) between C/C composite samples uncoated, coated with SiC, coated with SiC plus SiO_2-TiO_2 and coated with SiC plus SiO_2-Al_2O_3-LiO_2 shows that the sample coated with SiO_2-TiO_2 glass start to oxidise later and with slower

oxidation rate than any other, however, around 900°C the sample coated with SiO_2-Al_2O_3-LiO_2 started to exhibit the slowest oxidation rate.

The comparison between TG and DTG curves for Poco graphite samples (Figure 88) coated exactly in the same way described for the C/C composite samples shows that the results exhibited by the sample coated with SiC and SiC plus SiO_2-Al_2O_3-LiO_2 coincide. This means that the application of this coating did not improve the oxidation resistance already obtained when SiC was used alone, however, the degradation effect observed around 1100°C, when the SiO_2-TiO_2 coating was applied, was not found in this case.

CHAPTER V

DISCUSSION

The discussion of results follows the order of presentation of results in Chapter IV. The chapter starts with a discussion of the factors influencing the formation of dried gel coatings on carbon substrates (Section V.1). This is followed by consideration of the conversion of the gel coating to SiC and the steps taken to enhance the quality of the SiC coating (Section V.2). The chapter concluded by discussing the development and testing of the SiO_2-TiO_2 and SiO_2-Al_2O_3-LiO_2 glassy coatings (Sections V.3 and V.4).

V.1 - SiC COATING - CHARACTERIZATION AND GEL SELECTION

V.1.1- SCANNING ELECTRON MICROSCOPY (SEM)

without glycerol (DCCA)

It is well known that increasing the water/alkoxide ratio increases cross-linking density of the gels, changing them from long chain-like molecules to highly branched molecules (Scherer - 1988). Highly branched molecules generate lower density gels with larger pore diameters and lower shrinkage (Scherer - 1988, Klein - 1984, Sakka - 1980). This effect can explain the production of a finer mosaic structure, when the water/alkoxide ratio was increased for both solvents (ethanol and propanol) (Figures 37 - 40). Furthermore, it also

explains the increased porosity generated inside the gel particles when ethanol was used as the solvent. The last effect, was not observed when propanol was used as solvent because this alcohol is known to produce gels with finer pore size distribution than ethanol (Mackenzie - 1988, Chen - 1986) thus opposing and counter-balancing the effect of water/alkoxide ratio.

WITH GLYCEROL (DCCA)

The addition of glycerol, a high viscosity liquid, to the mixture reduceS the mobility of the long chain molecules and therefore limits their size and the extent of cross-linking. That effect can explain the unchanged mosaic structure found for both solvents with any water/alkoxide ratio when glycerol was added. As expected, the role of glycerol, as a drying control additive was confirmed in reducing pore size distributions and the mosaic particle's internal porosity (Ulrich - 1988, Hench - 1986) for both solvents used (ethanol and propanol) (Figures 41 - 44). Glycerol was more effective when propanol was used for the reasons discussed above.

The different morphologies of the dried gel coatings illustrated in Figures 45-47 are attributed to an interplay of two processes occurring during the sol-gel transformation: (i) gelation and ageing within the coating, which develops and strengthens an extended Si-O bond network, and (ii) interaction of the coating with the substrate during drying. If drying is more rapid than gelation and ageing, due to the vapour pressure of the liquid trapped inside the porosity or the gel structure, then coating-substrate adhesion occurs first and shrinkage stresses on subsequent gelation are partly accommodate by cracking within the gel particles. If gelation and ageing are more rapid than

drying, then shrinkage is partly accommodate by detachment of gel particles from the substrate and development of curvature.

V.1.2 - FOURIER TRANSFORM INFRA-RED (FT-IR)

When glycerol was not used, the spectra (spectra A in figures 48 and 49) for the dried gels 56 (solvent - ethanol) and 68 (solvent - propanol) showed both a broad region between 3800 cm^{-1} and 2900 cm^{-1} assigned, among other effects, to the Si-O-H stretching, and also a small difference in absorbance between the peaks **e** and **f**, corresponding respectively to Si-OH stretching and Si-O-Si stretching. However, when glycerol was introduced, the broad region cited above moved towards a peak (spectra B - Figures 48 and 49) and the difference between the absorbance of the peaks **e** and **f** was increased, particularly when propanol was the solvent. This means that the introduction of glycerol reduced the relative amount of Si-OH bonds and increased the relative amount of Si-O-Si bonds, i.e., the extent of polymerization increased with the addition of glycerol, particularly when propanol was used as solvent, and consequently a faster gelation should be expected in this case. To emphasise the effect of glycerol on the polymerization reaction the same broad area **a** and peaks **e**, **f** can be compared (Figures 50 and 51) for the spectra for the wet and dried gel 56 (solvent-ethanol, glycerol-not used) and gel 52 (solvent-ethanol, glycerol-used). The spectra for the gel 56 (Figure 50) show that the broad region **a** moves towards a peak only after drying and the absorbance of the peak **f** is greater than the absorbance of the peak **e**. However, for the gel 52 (Figure 51), when glycerol was used as DCCA, the spectra show that, even before drying, its polymerization was well

advanced, since there is not a large difference between the regions **a** and the peaks **e** and **f** in both spectra.

These FT-IR results support the argument that the introduction of glycerol in the mixture speeds up the gelation process, as was observed during the preparation of the gels. It is reasonable to suppose that the introduction of a low vapour pressure liquid in the mixture, such as glycerol, should delay the drying speed of the gel layer. The gels produced with glycerol consistently showed no internal cracks, little or no internal particle porosity and gel particles well bent out of the surface. These facts can be linked to support the argument that there is a competition between the drying speed and the gelation/ageing speed. If drying is faster than gelation, the dried gel coating should consist of flat particles with large cracks and porosity. On the other hand, if gelation is faster than drying the dried gel particles in the coating should be bent out of the surface of the substrate.

After firing of the coatings, the formation of SiC was clearly identified using FT-IR (Figure 52). The facility with which results can be obtained using FT-IR recommends the technique for characterizating this coating, however the results should be confirmed by X-Ray diffraction analysis.

V.1.3 - X-RAY DIFFRACTION ANALYSIS

No other phase but SiC was detected after that the gels were fired on the carbon surface (Figure 53). Thus there was no evidence for

crystalline forms of SiO_2 although the formation of amorphous SiO_2 cannot be ruled out despite the fact that no Si-O bond was detected by FT-IR (Figure 53). The formation of SiC in the gel coating occurs at a much lower temperature then is used for industrial production of SiC (2040 - 2600°C) (Kirk-Othmer - 1978). This may be attributed to the intimate contact between Si and C atoms at the molecular level in the dried gel which facilitates the reaction.

V.1.4 - X-RAY DISPERSIVE ANALYSIS

EDX showed that different gel compositions produced coatings of different quality. Bearing in mind the coating quality produced by the gel 56 (Figure 56A and 57A), one can see that the gels 32 (Figure 56B) and 80 (Figure 55C) did not produce a continuous SiC coating. These three gels were prepared with the same chemical composition (ethanol as solvent and no glycerol) except that the relative amount of water changed from 4 to 16 mol water/mol akoxide (gel 56 - 8 mol water/mol TEOS, gel 32 - 4 mol water/mol TEOS, gel 80 - 16 mol water/mol TEOS). These results corroborate those presented by Butts (Butts - 1988) who demonstrated that there are three types of wetting for a sol depending upon the water/alkoxide ratio. The best one was found when a medium water/alkoxide ratio, i.e. slightly above the stoichiometric ratio, (section III.3.2) is used. Lower standards of coating quality were also produced from gels 77, 89 and 92 when compared with gel 56. The gels 77 and 89 were produced using glycerol as DCCA and the low quality of their coating can be explained by the arguments presented in sections V.1.1 and V.1.2 (i.e., addition of glycerol results in a faster gelation speed than drying speed). The low quality of the coating

produced by gel 92 is explained by the high water/alkoxide ratio (four times above the stoichiometric value) used in its production.

V.1.5 - THERMOGRAVIMETRIC ANALYSIS

The TGA on samples submitted to multiple coating and firing procedures showed systematically that, at 920°C, the best results were achieved when the samples were fired just once. It is probable that thermocycling of the coatings following multiple firings causes cracking of the SiC layers resulting in a deterioration of oxidation resistance despite the increase in coating thickness. This argument is reinforced by the reduction in oxidation protection that was observed when a sample coated just once was fired twice (Figure 59). It was also observed that only samples coated with gels produced with 8 mol water/ mol TEOS plus gel 80 [produced with 16 mol water/mol TEOS (ethanol as solvent and no glycerol)] exhibited improved oxidation resistance when fired three times than when they were fired twice. As explained in Section V.1.4 this behaviour may be linked to a higher wettability of gels produced with medium water/alkoxide ratio. It is more difficult to explain the behaviour of the gel 80 but the morphology of the dried gel coating is closer to that of coatings produced with 8 mol water/mol TEOS (Section IV.1.2) than the morphology of any other.

A comparative analysis of the TG results (Figure 60) showed that after one firing the best oxidation protection was provided by the gels produced with 8 mol water/mol TEOS with ethanol (gel 56) or propanol (gel 68) and no glycerol. Figure 61 shows that only gels exhibiting a flat mosaic surface (gels 56, 80, 68, 32, 52 and 44), with

large internal cracks and defects, showed some oxidation protection after multiple firings. Thus, once again, it appears that the wettability of the carbon surface by the gels produced with medium water/alkoxide ratio and the competition between the drying and gelation speeds determine the level of oxidation protection afforded by the SiC coating produced by each gel.

V.2 - PRIMARY SiC COATING

V.2.1 - THE GEL ENHANCEMENT

The FT-IR spectra for the gels 8Ac, 56 and 8Eth (Figure 63) indicate that there is no detectable difference between the extente of polymerization of these gels, at room temperature, since the relative height of peaks **e** and **f** are very similar. However it is known, from the IR theory, that higher frequency position of peaks means stronger force between the atoms and this force can be calculated by the equation:

$$\gamma = 1307\ (K/\mu)^{1/2} \qquad (15)$$

where K - the force constant of the bond A-B

γ- the frequency in wavenumber

μ- the reduced atomic mass of A and B

It is also known from the IR theory that the intensity of an infrared band is proportional to the square of the change of the dipole moments during the vibration, i.e. stronger peaks in the infrared spectrum means higher dipole moments, therefore, the slight shift to

lower wave numbers in the position of peak **g** in the spectrum of the gel 8Ac, together with the increase in its intensity, when one moves from the gel prepared without acetone towards the gel prepared exclusively using acetone may indicate that the Si-O-Si bond is looser and exercising a more intense rocking movement. The increase in intensity of peak **g** can also result from an increase in concentration of Si-O-Si bonds, however it is unlikely that this is happening since there is no such large difference in peak **f** corresponding to Si-O-Si stretching.

The comparative TG and EDX results, between the gels **8Ac**, **56** and **8Eth** (Figures 64-66), leave no doubt that the oxidation resistance of the substrate was significantly improved with the inclusion of acetone in the mixture. The results show clearly the influence of the solvent on the quality of SiC coatings produced from gels and the important influence of a competition between the drying and gelation speeds as already discussed.

V.2.2 - CHARACTERIZATION ON ENGINEERING GRAPHITE GRADE AND C/C COMPOSITE SURFACES

The EDX images for Si, figures 67 and 68, show that a very thin SiC coating (7 μm) was produced on the surface of the KKarb C/C composite, in contrast with the thick coating (20 μm) roduced on Poco graphite. This suggests that a large amount of the gel, brushed on the surface, was consumed filling the cracks of the composite leaving only a small amount to form a coating. It is also possible that the adhesion

of the gel on the C/C composite surface is not so good as it is on graphite.

V.2 3 - THERMOGRAVIMETRIC ANALYSIS

The systematic improvement of the oxidation resistance exhibited by the Poco graphite samples with the increase of the number of firings (Figure 71) may be related to the increase of the thickness of the coating. No degradation of the oxidation resistance of coated Poco graphite was observed, when multiple firings were performed, as was noticed when using the electrode graphite as substrate. Possibly the cracks generated in the SiC layers, by successive thermocycling were mechanically closed by the thermal-expansion of the coating at 1200°C whrereas they were not closed at the lower testing temperature (920°C) used for the coated electrode graphite.

The SiC coating was not as beneficial on the C/C composite as it was on Poco graphite because its surface thickness was strongly reduced by consumption of the gel to fill the large cracks, as was discussed previously and as shown in figure 68. It may be possible to fill these cracks with SiC, by liquid impregnation with the sol 8Ac, followed by the production of a SiC coating, by brushing the gel. It would be worth investigating if thus procedure produces a thicker external coating and an improvement in the oxidation resistance of the C/C composite substrate and this technique should be investigated.

The transient increase in oxidation rate in the range 900-1200°C revealed by the DTG curve for uncoated Poco graphite (Figure 71) should be investigated more thoroughly. It may be due to the formation of tiny microcracks on the surface of the graphite due to thermal stresses generated by the very high heating rates used in the TG experiments (100°C/min). Formation of these cracks leads to an increase in active surface area of the graphite and so an increase in oxidation rate. The reduction in oxidation rate at the end of the transient may be attributed to closure of cracks at higher temperatures. A much smaller transient oxidation rate increase was observed for the uncoated KKarb C/C composite (Figure 72). The material is a pre-cracked body and thermal stresses can be accomodated to a large extent by opening up of pre-existing cracks leading to a smaller transient. This explanation is corroborated by the fact that coated samples of both materials, fired five times, do not exhibit the transient because the internal coated surface of microcracks are not available for reaction even when they are open (Figures 71, 72).

V.3 - SiO_2-TiO_2 COATING

V.3.1 - CHARACTERIZATION

Table 15 shows that there is a significant change in the SiO_2/TiO_2 ratio of the gel 2 after firing in argon atmosphere (firing procedure 1). This may be attributed to a carbothermic reduction of the SiO_2, producing SiO and CO. The carbon source for this reaction was probably the organic residues, e.g. solvent, trapped inside the coating during the drying process. The same residual carbon also leads to the

formation of TiC when this material is heated at temperatures around 1250°C, i.e. before the SiC reaction occurs. Firing the samples in air, at low temperatures (300°C) avoided the oxidation of the substrate and at the same time this undesirable effect, i.e. TiC formation, because the residual carbon trapped in the gel coating was burned-off.

V.3.2 - SCANNING ELECTRON MICROSCOPY AND X-RAY DISPERSIVE ANALYSIS

EDX images for the SiC/SiO_2-TiO_2 coatings (before heating to 1600°C) on KKarb C/C composite (Figure 76) show that Si penetrates pores and cracks deeply while Ti is retained at their entrance. The EDX image obtained after heating the SiO_2-TiO_2 glassy layer up to 1600°C (Figure 77) suggests that, if this coating did not reach the liquid stage, at least it was softened so that a larger penetration inside the porosity of the C/C composite was achieved. The images obtained for Ti on the C/C composite surface do not have sufficient resolution to evaluate the continuity of the coating, even after firing up to 1600°C, i.e. it cannot be positively confirmed that the melting point of this glassy layer was reached. However, when the top surface of this material was observed under SEM a very smooth surface with some defects (Figure 78) was observed. The small hole on the top surface of the C/C composite sample can be explained by the presence of volatile materials from either the SiC layers underneath (previously fired just up to 1450°C) or from the C/C composite itself. The lateral side of the sample (where the coating is not as thick as in the top surface due to brushing difficulties in this very small area) showed cracks on the glassy coating in the same position where defects on C/C composites

are usually found. This suggests that the microstructural defects in the C/C composite could be responsible for the damage to the coatings, instead of a mismatch between the CET values of the coating and the substrate. The well known mismatch between the CTE of the carbon fibers and the matrix could explain the cracks found running along several fiber bundles-matrix interfaces (Figure 80).

V.3.3 - THERMOGRAVIMETRIC ANALYSIS

There is a distinct improvement in the oxidation resistance of the KKarb C/C composite coated with SiC/SiO_2-TiO_2 layers compared with the composite coated only with SiC layers (Figure 82). The improvement of the oxidation resistance can be explained by the penetration of this material inside of the large cracks of the substrate.

The changes in oxidation resistance of Poco graphite when coated with SiC and SiO_2-TiO_2 are difficult to explain. Poco graphite is well known for its extreme homogeneity and low open porosity which therefore did not favour penetration of the SiO_2-TiO_2 glassy coating inside its pores even when it was heated to 1600°C. The decrease in oxidation resistance of the sample coated with SiC and SiO_2-TiO_2 (when compared with the sample coated with SiC alone) may be explained by damage to the ceramic layer, during the cooldown from the maximum heat treatment temperature.

V.4 - SiO_2 - Al_2O_3 - LiO_2 COATING

V.4.1 - CHARACTERIZATION

It appears from X-Ray diffraction (Figure 84) that a lithium-aluminium-silicate was formed on the SiC/C/C composite substrate, although it would be convenient to identify positively which one was formed to determine precisely its melting point. As noted in Chapter IV the techniques used in this project were not suitable for positive identification of Li-coating glasses and it would be convenient, for future work, to find for a suitable method of analysing this coating on a carbon/SiC substrate.

The SEM photographs (Figure 85) showed that a vitreous coating with several hair-line cracks was produced. These defects may result from thermal stresses generated during either heat treatment, or the firing procedure. It is possible that a more vitreous coating, i.e. with a higher concentration of SiO_2, but still able to produce ß-Eucryptite crystals, such as 75%wt of SiO_2, 10%wt of Al_2O_3 and 15%wt of LiO_2 (Figure 36), may be more resistant to cracking. This SiO_2-Al_2O_3-LiO_2 glass-ceramic coating exhibited a deeper and more uniform penetration inside of the porosity of the C/C composite samples than the SiO_2-TiO_2 glass (Figures 75 and 86). As C/C composite cracks should be almost completely open when the melting point of the SiO_2-Al_2O_3-LiO_2 was achieved (1000°C), this penetration should be favoured.

V.4.2 - THERMOGRAVIMETRIC ANALYSIS

The oxidation resistance at 1200°C of KKarb C/C composite coated with SiC/SiO_2-Al_2O_3-LiO_2 was slightly better than that found for the composite coated with SiC/SiO_2-TiO_2 (Figure 87) and thus the combination of SiC with SiO_2-Al_2O_3-LiO_2 produced the best coating on the KKarb material from the point of view of oxidation resistance. The SiO_2-Al_2O_3-LiO_2 layer was superior to the SiO_2-TiO_2 layer in its performance on Poco graphite (Figure 88) although its performance was comparable to that of the SiC coating. As noted above the reasons for this unusual behaviour is not clear.

CHAPTER VI

SUMMARY AND CONCLUSIONS

In this final chapter the main findings and principal conclusions of this work are summarised and where appropriate suggestions are made for further work.

The critical properties required of an oxidation resistant coating on carbon, revealed by a literature review of existing coating methods are: (i) low coefficient of thermal expansion (CTE) to match the CTE of the carbon substrate for the operating temperature range; (ii) low permeability to oxygen diffusion and (iii) chemical stability in contact with the carbon substrate. These factors were used in a material selection exercise which reduced the list of potential single coatings on carbon materials to HfC, Mo_5Si_3, SiC, BN, Ta_2O_5, SiO_2. If other compounds researched in previous work are added to this list, it should include HfO_2, Al_2O_3, Si_3N_4, TaN, Si, HfTi, Cr_3C_2 and ZrTi but of these materials SiC was identified potentially as the most cost-effective coating material.

Plasma arc spraying was used to produce coatings of Ni-Cr-Al-Y and Al (usual bond coatings applied with this technique), SiC, Ni-Cr-Al-Y and SiC, Si, Si and SiC and Cr_3C_2. The coatings were porous and it proved impossible to coat SiC satisfactorily; therefore this method was abandoned. In future work this method may be improved by vacuum application of the coating followed by the use of the gas pressure bonding to improve the intimate contact with the substrate and to reduce porosity and oxygen trapped in the coating. However the

prospects for these improvements on the method are not good since they have been tried by researchers in the seventies only with limited success. One of the reasons for the method to be dismissed is that it appears to be impossible to spray SiC satisfactorily also, its low efficiency will increase substantially the cost of applying more sophisticated refractory coatings on carbon materials. For these reasons, the alternative sol-gel method was investigated.

A SiC coating was developed from an acid-catalysed tetraethyl ortho silicate (TEOS) sol-gel using a phenolic resin as a carbon source by firing to 1450 °C. The SiC formation was identified by FT-IR and X-Ray diffraction, while the SiC coating formation was followed by X-Ray dispersive analysis. A study of the influences of the sol formulation on the oxidation resistance of the SiC coating at 920°C showed that the quality of the coating was improved if the rate of gelation/ageing was slower than the rate of drying. When glycerol was not used as drying chemical control additive (DCCA), the increase in the water/alkoxide ratio produced a finer mosaic structure for both solvents (ethanol and propanol) but the internal particle's porosity increased only when ethanol was used as the alkoxide solvent. When glycerol was used no change was observed in the mosaic structure for both solvents but the particle's porosity became more uniform with ethanol and disappeared when propanol was used. FT-IR was demonstrated to be an efficient technique to follow the gelation of the coating on the carbon substrate by comparing the relative height of the peaks resulting from the stretching of Si-OH (around 950 cm^{-1}) and Si-O-Si (around 800 cm^{-1}) bonds.

Using this principle, an optimised SiC coating was developed with a molar water/TEOS ratio of 8:1 and acetone as the solvent. The water/alkoxide ratio modifies the cross-linking of the molecules during polymerization and is related to the wettability of the substrate, while the drying and gelation speeds are related to the adhesion of the gel to the substrate. The best composition was found with medium water/alkoxide ratio (8:1) able to dry fast and to gel slowly (both effects were observed with acetone as the solvent).

Since the SiC coating was cracked, as a result of thermocycling, further improvements in oxidation resistance were sought by developing, using sol-gel methods, multilayer coatings with a glassy overlayer. These coatings were applied to a fine grained Poco graphite and a 2-D carbon-carbon (C/C) composite, the first being a monolithic graphite, with very small open porosity, and the second a C/C composite partially densified by liquid impregnation and therefore exhibiting large cracks and porosity.

Based upon a literature survey, a SiO_2-TiO_2 glass and a SiO_2-Al_2O_3-LiO_2 glass-ceramic coating were selected to enhance the oxidation resistance of the carbon material, previously coated with a SiC layer, because they melt around 1600°C and 1000°C respectively and they both exhibit low CTE and low permeability to oxygen diffusion.

For the SiO_2-TiO_2 glass a firing procedure was developed which inhibited the formation of undesirable TiC that was detected by X-Ray diffraction when this glassy coating was fired only under Ar atmosphere. To eliminate the residual carbon in the SiO_2-TiO_2 sol-gel

coating, that was assumed to be the source for the TiO_2 reduction without oxidising the carbon substrate, the coated carbon material was fired under air up to 300°C (with a soaking time of 12 hours) followed by a firing under Ar up to 1450°C. This procedure avoided the formation of TiC that was confirmed by the elimination of its peaks in the X-Ray diffractograms. The SiC/SiO_2-TiO_2 coating, after firing to 1600°C improved the oxidation resistance at 1200°C of the C/C composite due to its ability to penetrate cracks deeply, but it produced no additional benefit, compared to the SiC coating, when applied to the monolithic Poco graphite. This may result from the 20 μm thick SiC coating on Poco graphite being to thin. The application of the gel on the carbon surface by brushing can be optimized to produce thicker SiC coatings with fewer firings. While a SiC coating of around 20 μm thick was produced on the top surface of a Poco graphite sample (Figure 69) a coating around 30 μm thick was produced inside the sample suspension hole (Figure 71) with the same number of firings.

The SiC/SiO_2-Al_2O_3-LiO_2 coating slightly improved the oxidation resistance of the C/C composite at 1200°C, compared to the SiC/SiO_2-TiO_2 layer, and was also superior to the SiC/SiO_2-TiO_2coating on Poco graphite where no evidence of improvement on the oxidation resistance was observed when the glassy layer was applied when compared with the SiC coating alone. The modification of the chemical composition of the SiO_2-Al_2O_3-LiO_2 glass-ceramic coating by increasing the relative amount of SiO_2, as suggested in chapter V, may improve the oxidation protection afforded by this coating.

The use of glassy and glass-ceramic coatings combined with SiC coatings showed a marked enhancement of the oxidation resistance of the C/C composite substrate by filling its cracks and defects. It may be that a previous infiltration of these materials in the sol stage to fill the cracks, followed by the production of a coating on the C/C composite surface, will improve the oxidation resistance of the substrate still further. It may also be possible to apply the gel during the manufacturing process between the pre-preg layers or during winding. If SiO_2-TiO_2 is to be used it must be heat treated up to 1600°C, at least, to ensure full melting and in this case the SiC coatings previously applied should be fired up to the same temperature to eliminate completely residual volatiles that may damage the upper coating.

If coatings of SiO_2-TiO_2 glass and SiO_2-Al_2O_3-LiO_2 glass-ceramic were produced on SiC carbide using the sol-gel technique, it would be interesting in future work to determine the oxidation protection that can be obtained from a multilayer system using layers of both materials cited above, separated by an intermediate SiC layer, e.g. SiC/SiO_2-TiO_2/SiC/SiO_2-Al_2O_3-LiO_2, and to verify if any interaction between the two glassy layers would occur.

In summary this work has shown for the first time that SiC coatings can be formed on carbon substrates using sol-gel methods and that these coatings confer significant oxidation resistance to different carbon substrates. The work has also shown for the first time that it is possible to develop multilayer SiC/glassy coatings by the sol-gel method. The production of SiC/SiO_2-TiO_2 and SiC/SiO_2-Al_2O_3-LiO_2

coatings on two carbon substrates was demonstrated and these coatings were shown to give enhanced oxidation resistance when applied to a carbon-carbon composite. Finally, the sol-gel method has been shown to be a flexible, low-cost technique for producing oxidation-resistant coatings on carbon materials. With further development, it is expected that coatings produced using sol-gel methods will confer oxidation protection which is comparable to that produced by established processes such as pack methods.

TABLES

TABLE 1

Comparative price for buying 300 cm^3 of the selected refractory materials to be sprayed by the plasma arc spray method.

SiC	£1.00
Al_2O_3	£6.00
Si	£36.00
B_4C	£70.00
Si_3N_4	£137.00
Cr_3C_2	£196.00
TiB_2	£219.00
BN	£220.00
SiO_2	£581.00
Ta_2O_5	£1,327.00
HfO_2	£1,704.00
HfC	£3,486.00
TaN	£6,403.00
HfTi	(very expensive)

TABLE 2

Comparative weight gain between samples sprayed with a coating of Si and Si plus SiC.

sample nº	weight gain	
	Si	Si50%+SiC50%
37	0.255g	
38	0.268g	
39	0.277g	
40	0.294g	
41	0.277g	
42		0.105g
43		0.095g
44		0.106g
45		0.107g

TABLE 3

Properties of xerogels dried at 25 and 600°C for different catalysts (Pope - 1986).

25°C

Catalyst	Volume shrinkage %	Bulk density (g/cm^3)	Apparent density (g/cm^3)	Per cent porosity
HOAc	84.0	1.32	1.33	0.7
HCl	81.3	-	-	-
HNO_3	79.9	1.14	1.16	1.7
H_2SO_4	71.6	-	-	-
HF	78.4	0.54	1.24	56.7
NH_4OH	67.8	0.49	1.13	57.0
no catalyst	87.5	0.95	2.09	54.6

600°C

Catalyst	Volume shrinkage %	Bulk density (g/cm^3)	Apparent density (g/cm^3)	Percent porosity
HOAc	2.08	2.12	1.9	
HCl	85.2	2.06	2.12	1.9
HNO_3	85.2	1.82	2.02	10.0
H_2SO_4	80.0	1.46	2.12	31.0
HF	82.7	0.71	2.13	67.0
NH_4OH	71.7	0.70	2.21	68.0
no catalyst	-	1.25	2.21	43.4

TABLE 4

Gel production from different precursors (Chen - 1986).

Sample		Starting compounds	Solvents	Catalyst	Results
(A)	(1)	$Si(OCH_3)_4$	C_2H_5OH	HCl	transparent gel
	(2)	$Si(OC_2H_5)_4$	C_2H_5OH	HCl	transparent gel
	(3)	$Si(OC_4H_9)_4$	C_2H_5OH	HCl	translucent gel
	(4)	$Si(CH_3)(OC_2H_5)_3$	C_2H_5OH	HCl	precipitation
	(5)	$Si(OOCCH_3)_4$	C_2H_5OH	HCl	transparent gel
	(6)	H_2SiO_3	C_2H_5OH	HCl	precipitation
(B)	(7)	$Si(OCH_3)_4$	CH_3OH	HCl	transparent gel
	(8)	$Si(OC_2H_5)_4$	CH_3OH	HCl	transparent gel
	(9)	$Si(OC_4H_9)_4$	CH_3OH	HCl	transparent gel
	(10)	$Si(CH_3)(OC_2H_5)_3$	CH_3OH	HCl	precipitation
	(11)	H_2SiO_3	CH_3OH	HCl	precipitation
(C)	(12)	$Si(OCH_3)_4$	n-C_3H_7OH	HCl	transparent gel
	(13)	$Si(OC_2H_5)_4$	n-C_3H_7OH	HCl	transparent gel
	(14)	$Si(OC_4H_9)_4$	n-C_3H_7OH	HCl	translucent gel
	(15)	$Si(CH_3)(OC_2H_5)_3$	n-C_3H_7OH	HCl	translucent gel
	(16)	H_2SiO_3	n-C_3H_7OH	HCl	with some ppt precipitation

TABLE 5

Gelation characteristics of successfully prepared gels listed in Table 4 (Chen - 1986).

Sample	Starting compounds	Solvents	Gelation time (h)	Initial volume (cm3)	Volume at gelation (cm3)	Volume shrinkage	Oxide content (g/cm3)
(A) (1)	$Si(OCH_3)_4$	C_2H_5OH	152	24.0	16.7	30	0.192
(2)	$Si(OC_2H_5)_4$	C_2H_5OH	242	27.7	17.3	37	0.186
(3)	$Si(OC_4H_9)_4$	C_2H_5OH	243	36.0	30.6	15	0.108
(4)	$Si(OOCCH_3)_4$	C_2H_5OH	1	25.0	25.0	0	0.132
(B) (5)	$Si(OCH_3)_4$	CH_3OH	44	16.5	12.0	30	0.324
(6)	$Si(OC_2H_5)_4$	CH_3OH	108	21.0	14.7	30	0.221
(7)	$Si(OC_4H_9)_4$	CH_3OH	64	29.0	27.7	4	0.117
(C) (8)	$Si(OCH_3)_4$	n-C_3H_7OH	131	24.2	21.5	11	0.150
(9)	$Si(OC_2H_5)_4$	n-C_3H_7OH	246	28.3	23.5	17	0.138
(10)	$Si(OC_4H_9)_4$	n-C_3H_7OH	550	37.5	29.5	21	0.110

TABLE 6

Coefficients of thermal expansion for low expansion glass-ceramic materials (Corning Glass Works - 1970).

Flux composition					Fused bonding material - Average Thermal Expansion (cm/cm °C. X 10^{7})			
Example nº	SiO_2	Al_2O_3	B_2O_3	Li_2O	Cycle A	Cycle B	Cycle C	Cycle D
1	60.0	33.0	-	7.0	2.7	3.5	2.6	-
2	67.5	26.8	-	5.7	2.8	3.1	2.8	-
3	75.0	20.6	-	4.4	0.8	2.3	1.6	4.9
4	60.0	16.0	17.0	7.0	4.4	7.0	6.7	-
5	67.5	13.0	14.0	5.5	5.1	4.0	6.5	7.8
6	75.0	10.0	10.5	4.5	5.4	5.3	6.1	-
7	60.0	16.0	-	24.5	3.2	1.3	5.6	-
8	67.5	13.0	-	19.5	2.3	3.7	4.3	-
9	75.0	10.0	-	15.0	0.7	-1.2	0.0	-
10	60.0	16.0	5.6	18.4	1.1	3.7	5.6	3.2
11	67.5	13.0	7.0	12.5	0.8	3.6	3.3	2.0
12	60.0	16.0	11.4	12.6	2.4	3.4	4.1	3.4
13	60.0	21.6	11.4	7.0	4.2	3.5	5.8	-
14	67.5	20.0	7.0	5.5	4.4	4.3	5.6	-
15	60.0	27.4	5.6	7.0	3.4	4.7	4.9	5.2
16	60.0	21.7	-	18.3	1.0	1.6	1.9	1.9
17	67.5	20.0	-	12.5	4.0	4.6	3.8	3.5
18	60.0	27.3	-	12.7	3.1	3.4	3.9	2.8
19	60.0	21.8	5.6	12.6	2.6	3.3	2.6	2.6
20	67.5	17.6	4.7	10.1	2.8	3.1	4.2	3.2

A - Heat to 1000 °C at 80 °C/h, hold 10 hours
B - Heat to 1000 °C at 360 °C/h, hold 10 hours
C - Heat to 960 °C at 360 °C/h, hold 10 hours
D - Heat to 1040 °C at 360 °C/h hold 10 hours

TABLE 7

pH of the ten acid-catalysed sols produced in this study to generate and to optimise a SiC on carbon materials.

gel number	pH
32	1.4
44	1.3
52	1.8
56	1.9
65	1.8
68	1.8
77	2.1
80	2.2
89	2.0
92	2.1

TABLE 8

Molar composition and appeareance of the base-catalysed gels.

gel number	H_2O/TEOS	NH_4OH/TEOS	pH	gel appeareance
300	2	1	8.9	precipitate
301	2	0.5	8.8	precipitate
302	2	0.1	9.3	floculate
303	2	0.02	7.9	floculate
304	4	0.5	9.9	precipitate
305	4	0.1	9.5	floculate
306	4	0.02	8.5	powdery
307	16	0.05	9.3	precipitate
308	16	0.02	8.5	2 phases

TABLE 9

Assignment of the main peaks observed at the FT-IR spectrum for the gel coating on graphite substrate.

peak nº	frequency - cm^{-1}	assignment
a	3660cm^{-1}	stretching of substituted benzene ring + stretching of the solvent (primary alcohol) + stretching of water + stretching of Si-O-H
b	1640 cm^{-1}	overtone Si-O
c	1300cm^{-1}	stretching of substituted benzene ring
d	1080 cm^{-1}	stretching of <-SiO-><-Si
e	950 cm^{-1}	stretching of Si-OH
f	800 cm^{-1}	stretching of <-Si-O-Si->
g	455 cm^{-1}	deformation of Si-O-Si-O

TABLE 10

Comparison between the absorbance of the peaks e and f for the dried gels produced using ethanol and propanol with and without glycerol.

gel	solvent/additive	peak e	peak f	absorbance ratio
56	ethanol/no glycerol	0.24528	0.26264	0.93
52	ethanol/glycerol	0.15642	0.18093	0.86
65	propanol/no glycerol	0.1748	0.1877	0.93
68	propanol/glycerol	0.0785	0.1475	0.53

TABLE 11

Comparison between the absorbance of the peaks e and f for the gels produced with ethanol, with and without glycerol, before and after drying.

gel	solvent/additive	gel condition	peak e	peak f	absorbance ratio
56	ethanol/no glycerol	wet	0.2877	0.2859	1.006
56	ethanol/no glycerol	dried	0.1678	0.1880	0.89
52	ethanol/glycerol	wet	0.7017	0.7263	0.97
52	ethanol/glycerol	dried	0.6371	0.6616	0.96

TABLE 12

X-Ray standard and obtained diffraction lines for graphite and SiC.

Graphite		SiC	
standard	obtained	standart	obtained
3.35	3.33	2.53	2.51
2.03	2.07	1.54	1.54
1.67	1.68	1.31	1.31
1.15	1.22	-	-

TABLE 13

Comparative oxidation behaviour of the gels 44 and 56 fired once, twice and three times.

gel	number of firings	weight loss after 30min (%)
44	1	23.5
44	2	25.5
44	3	31.5
56	1	14.5
56	2	21.0
56	3	20.0
uncoated	-	34.5

TABLE 14

Firing procedures for the SiO_2-TiO_2 layer.

firing procedures	dwells and soaking times
1	steps under Ar - 50°C (1h), 125°C (24h), 250°C (24h), 400°C (48h), 750°C (4h), 1250°C (12h), 1450°C (12h)
2	a)steps under air 50°C (1h), 125°C (24h), 250°C (24h), 400°C (24h) b)steps under Ar 400°C (24h), 750°C (4h), 1250°C (12h), 1450°C (12h)
3	a)steps under air 50°C (1h), 125°C (12h), 300°C (12h) b)steps under Ar 400°C (12h), 750°C (4h), 1250°C (12h), 1450°C (1h)

(constant heating rate - 2°C/min- for all the firing procedures)

TABLE 15

Relative percentage of SiO_2/TiO_2 before and after firing as a function of the firing procedure.

GEL	Calculated	EDX		change %	Firing procedure
		before firing	after firing		
2	81.3/18.7	79.1/20.9	26.1/74.0	254	1
2	81.3/18.7	-	73.8/26.2	-	2
2	81.3/18.7	84.8/15.2	77.3/22.7	49	3
3	88.2/11.8	90.1/9.9	90.3/9.7	2.0	3
6	92.5/7.5	92.9/7.1	94.2/5.8	18	3
7	90.5/9.5	91.7/8.3	91.8/8.2	1.2	3

change % =[ABS(TiO_2 before firing - TiO_2 after firing)/TiO_2 before firing]x100

TABLE 16

X-Ray standard and obtained diffraction lines for TiC

standard peaks	obtained peaks
2.50	2.48
2.16	2.12
1.53	1.52
1.30	1.30

TABLE 17

X-Ray standard and obtained lines for graphite, two Lithium-aluminium-silicates and the lithium aluminium-silicate coating produced using the sol-gel technique.

graphite	$Li_2Al_2Si_2O_8$	α-Eucryptite	sol-gel
standard	standard		obtained
3.33	3.96	3.95	4.00
2.03	**3.16**	**3.37**	**3.17**
1.67	2.74	4.01	-

FIGURES

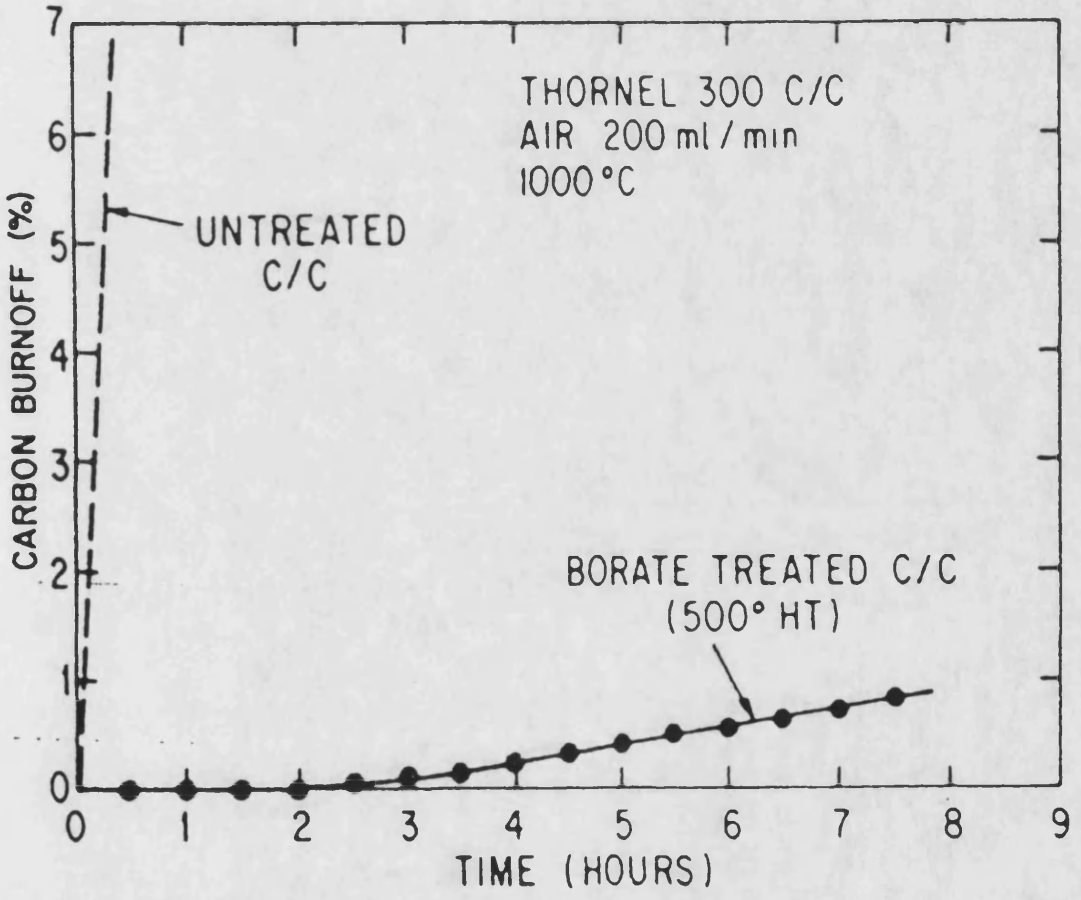


FIGURE 1 - Effect of borate treatment on gasification of Thornel 300 C/C composite (Union Carbide Co.) in air at 1000°C. Percent weight losses vs time (McKee[2] - 1986).

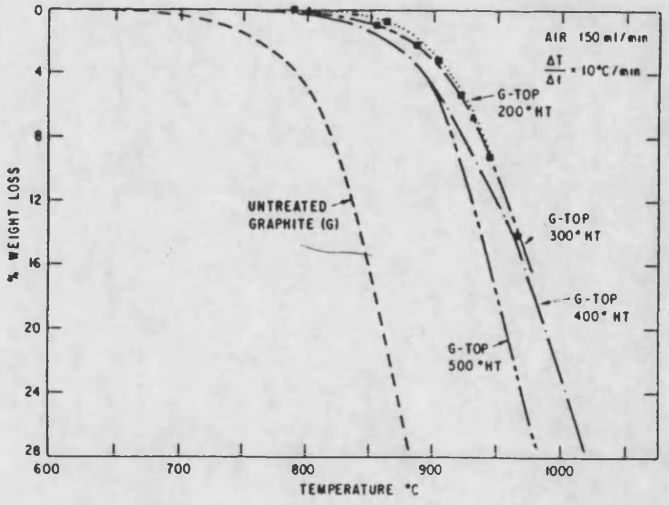


FIGURE 2 - Oxidation of graphite and tri-octyl phosphate-treated graphite as a function of heat treatment temperature. Weight losses vs temperature in flowing air. Temperature rise rate = 10°C/min (McKee[1] - 1984).

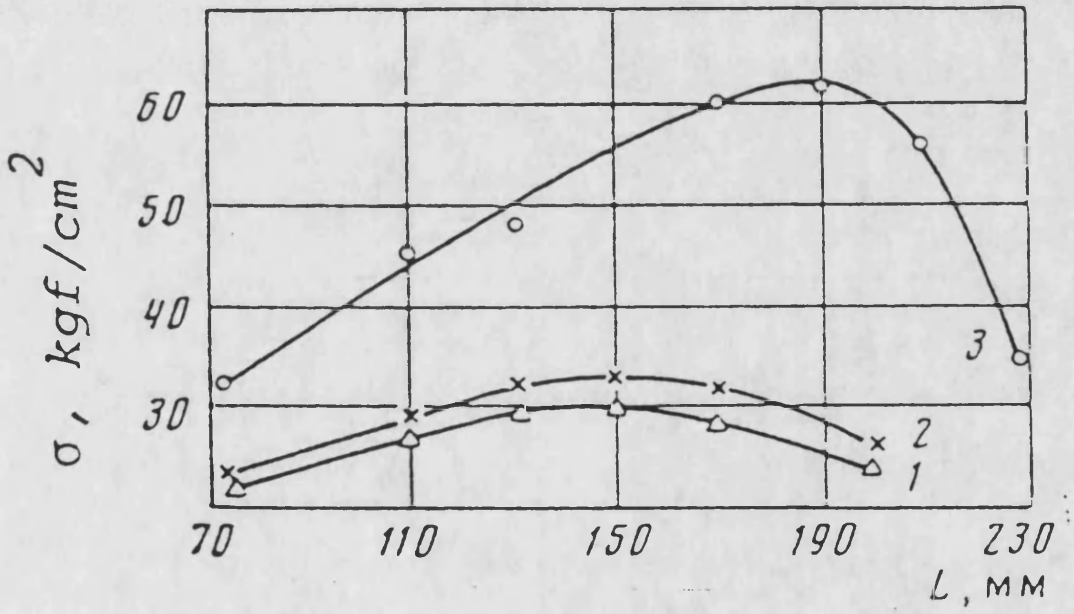


FIGURE 3 - Dependence of the bonding strength of coating with substrate on spraying distance for aluminium content of alumina off 30% (1), 50% (2), and 70% (3) (Konokotin - 1983).

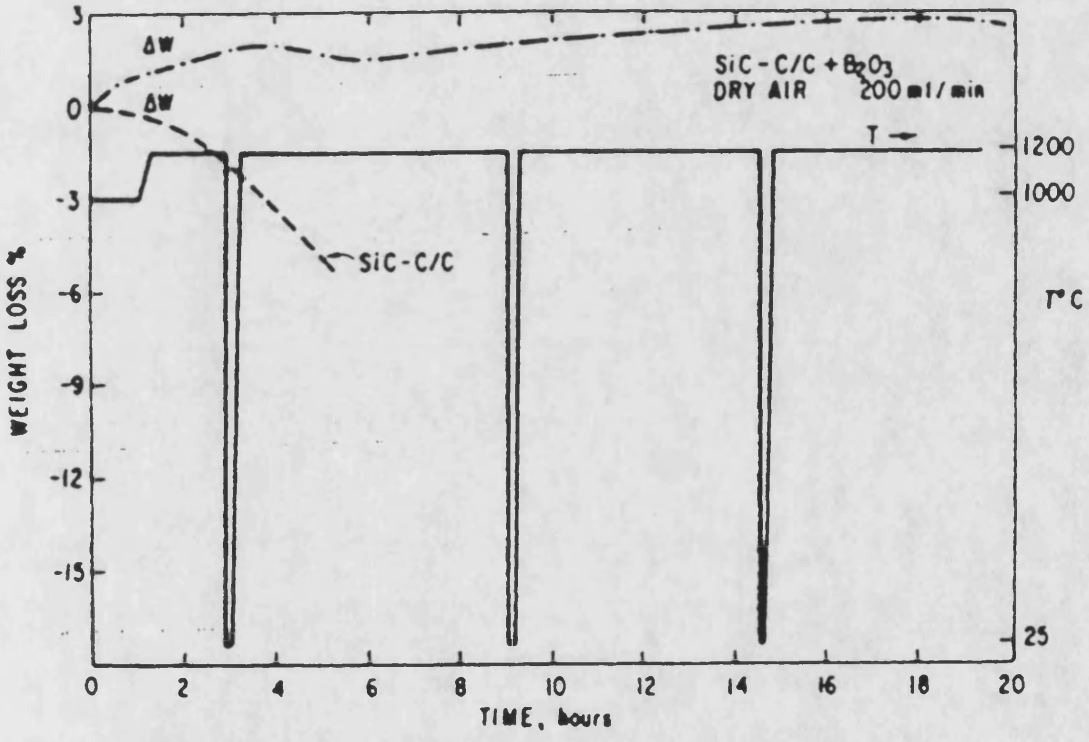


FIGURE 4 - Oxidation behavior of SiC-C/C specimens, before and after coating with borate, on heating in dry flowing air at 1200°C (with intermittent cooling to 25°C). Weight change vs. time (McKee - 1987).

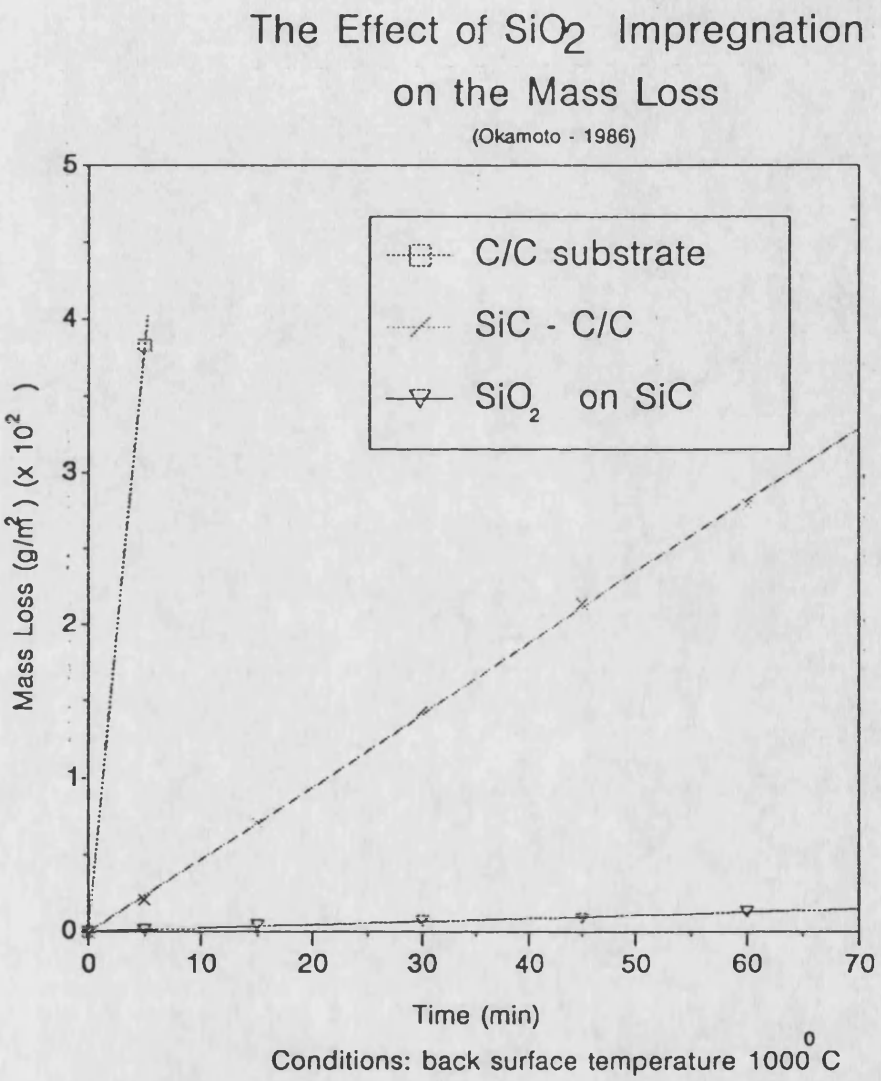


FIGURE 5 - The effect of SiO_2 impregnation on the mass loss (Okamoto - 1986).

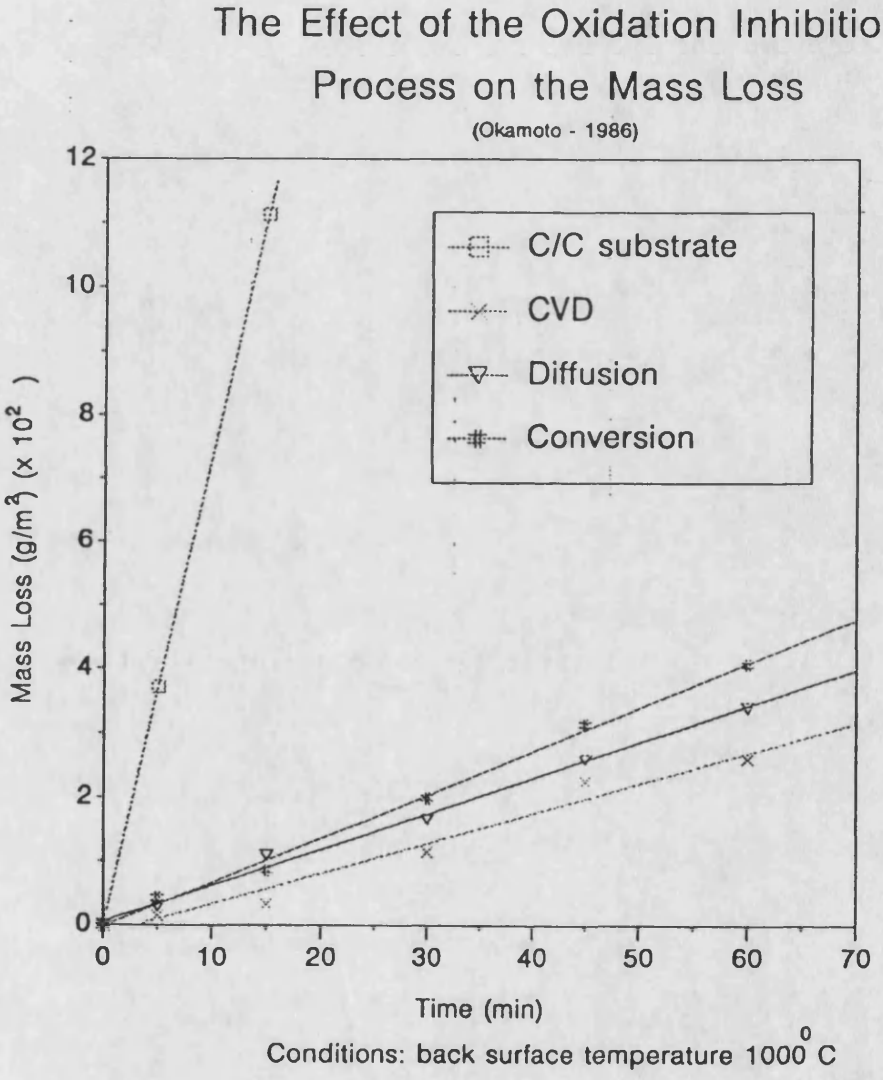


FIGURE 6 - The effect of the oxidation inhibition process on the mass loss (Okamoto - 1986).

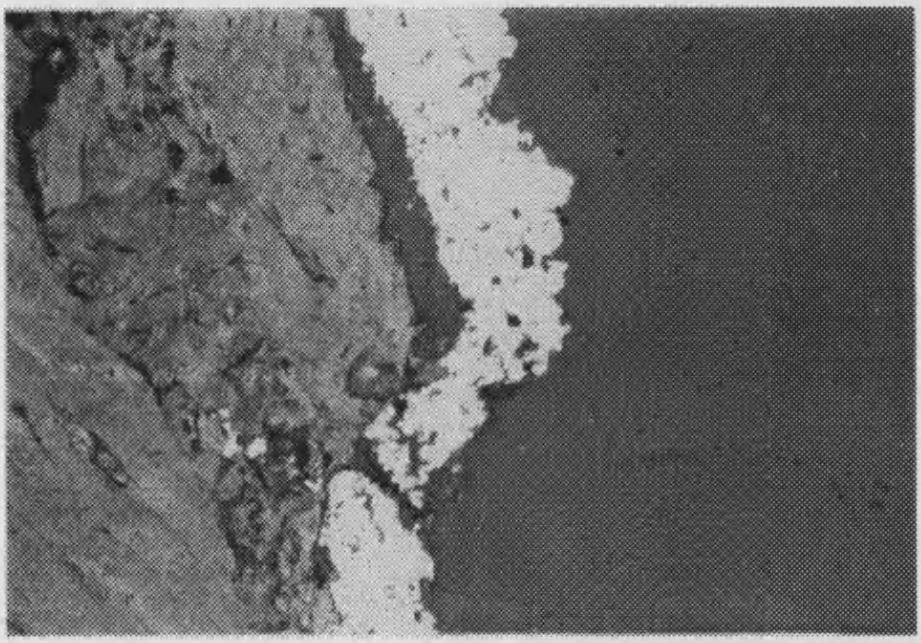


FIGURE 7 - Defect on the coating at the edge of the sample.

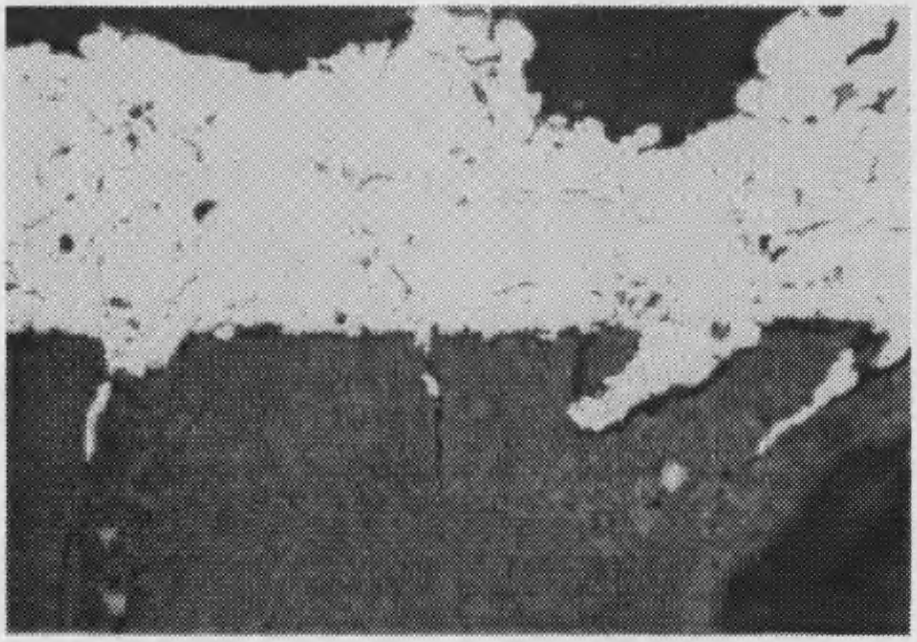


FIGURE 8 - Coating of Ni-Cr-Al-Y on graphite showing the penetration in the porosity

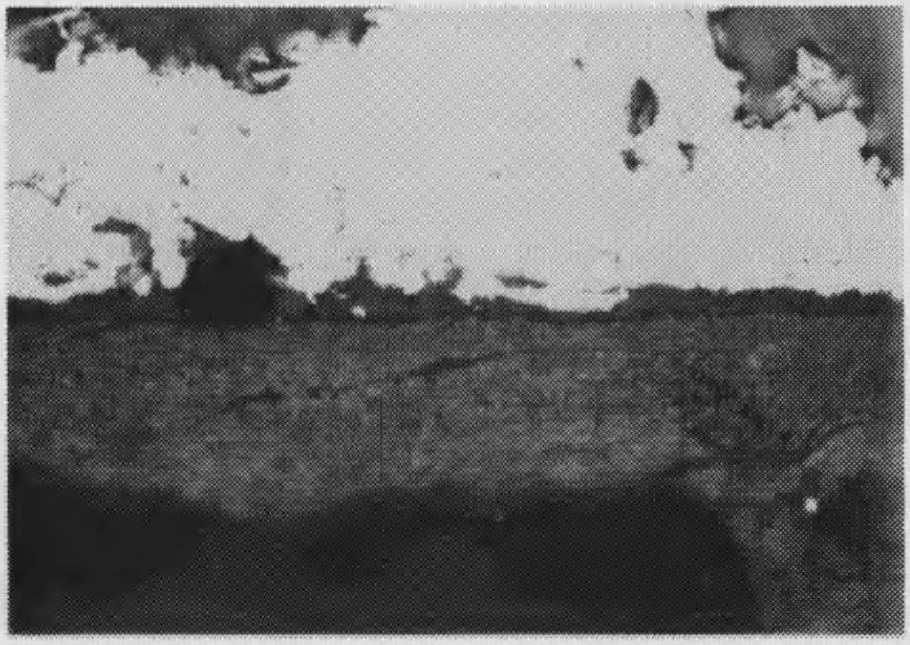


FIGURE 9 - Coating of Ni-Cr-Al-Y on graphite - defect on the coating

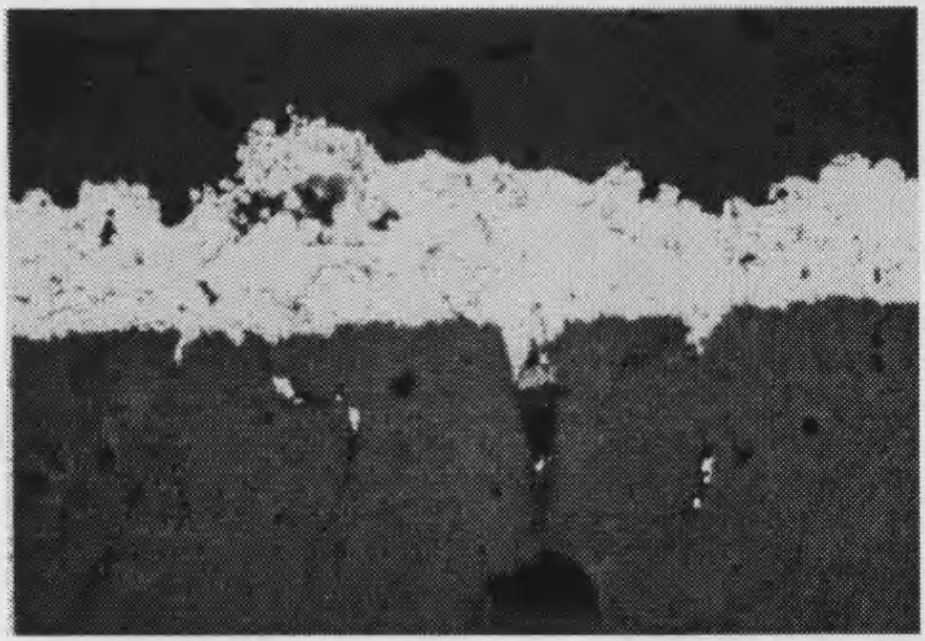


FIGURE 10 - Coating of Ni-Cr-Al-Y on graphite, with the substrate preheated at 340°C, exhibiting good adhesion to the substrate.

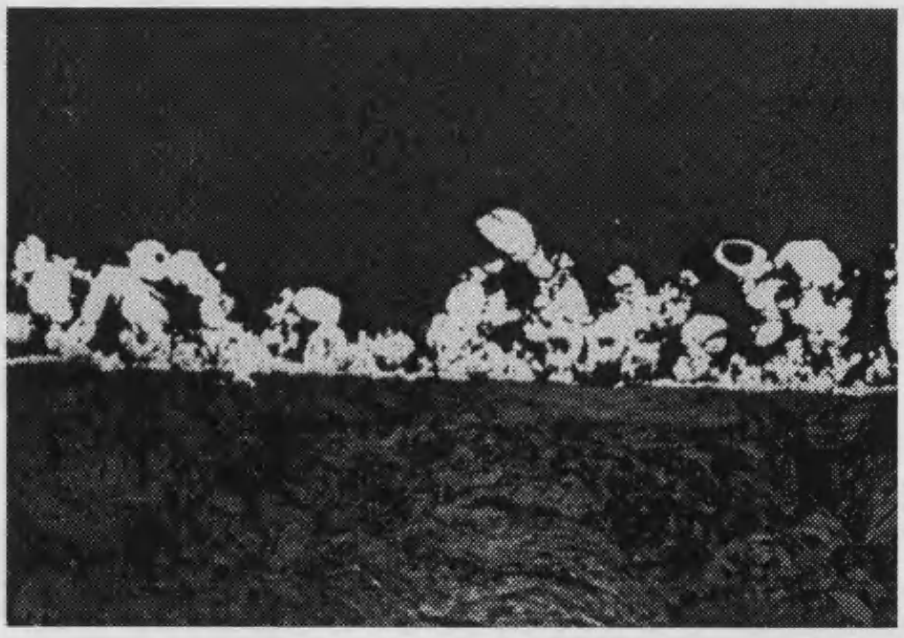


FIGURE 11 - Coating of aluminium on graphite showing a large porosity and a lack of continuity.

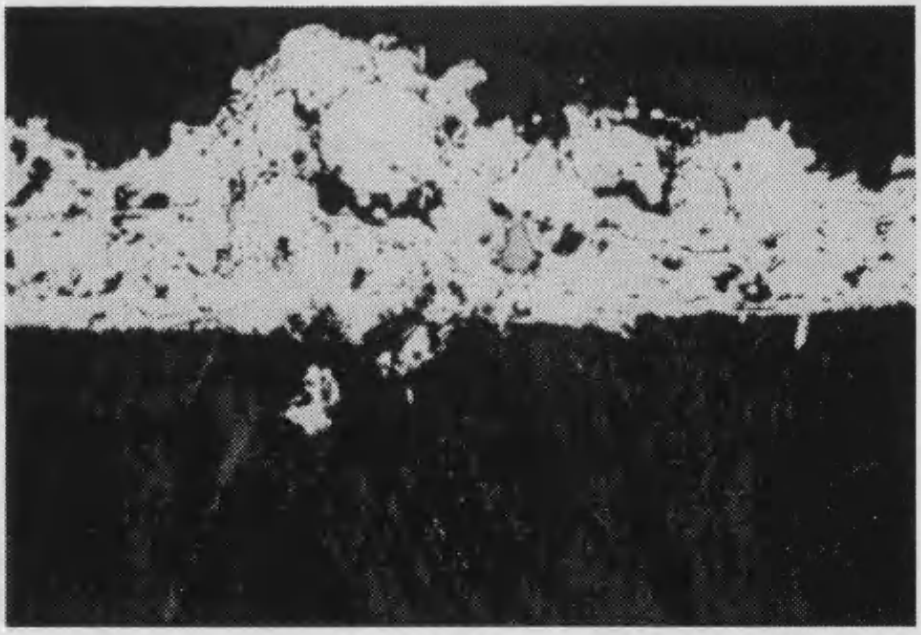


FIGURE 12 - Coating of Ni-Cr-Al-Y, and few trapped SiC particles, on graphite.

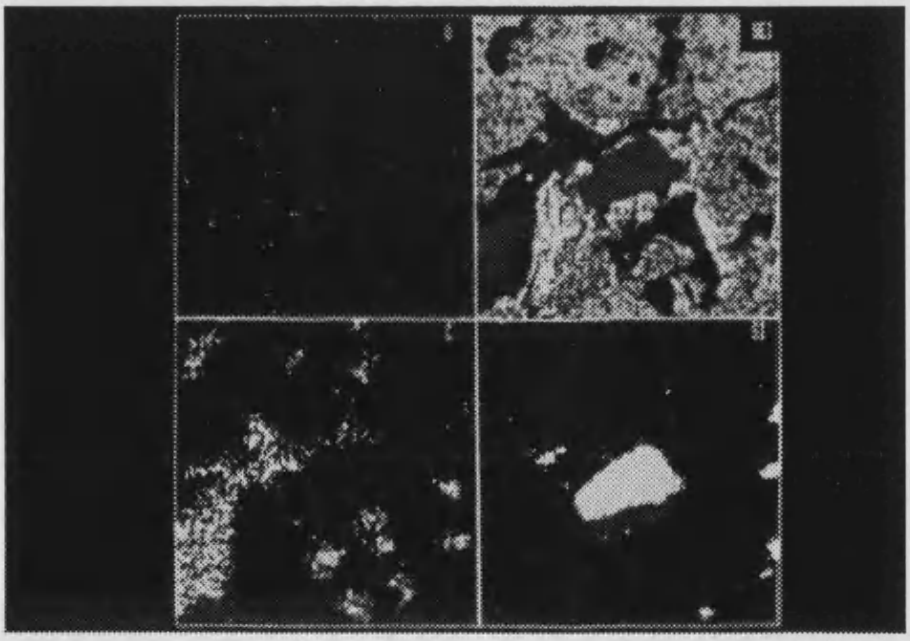


FIGURE 13 - Particle of SiC, identified by EDX, trapped inside the carrier Ni-Cr-Al-Y coating on graphite.

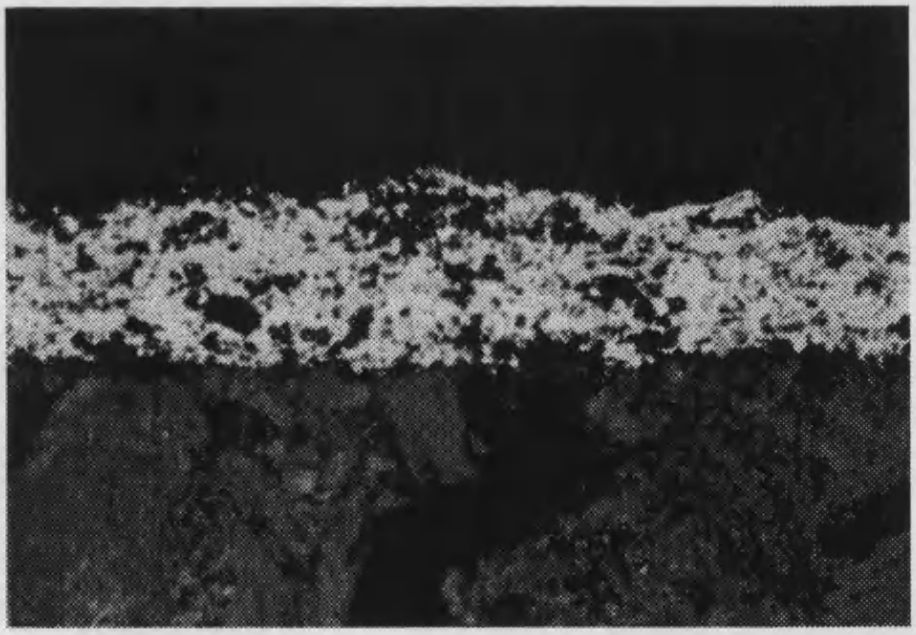


FIGURE 14 - Coating of Si on graphite where a large porosity is observed.

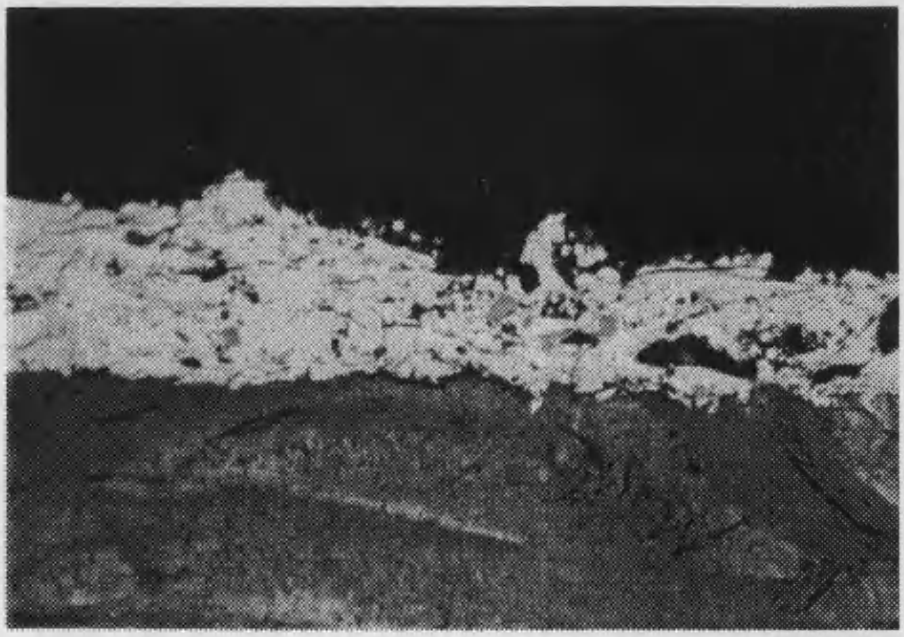


FIGURE 15 - Coating of Si and SiC on graphite where Si was used as a carrier

FIGURE 16 - Coating of Cr_3C_2 on graphite.

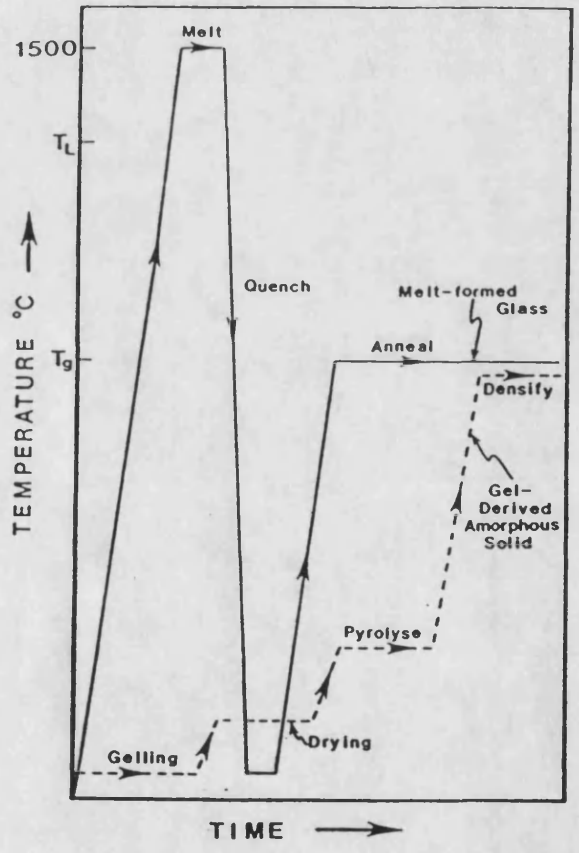


FIGURE 17 - Comparison of the processing of melt-derived glasses and gel-derived "glass-like solids" (Mackenzie - 1988)

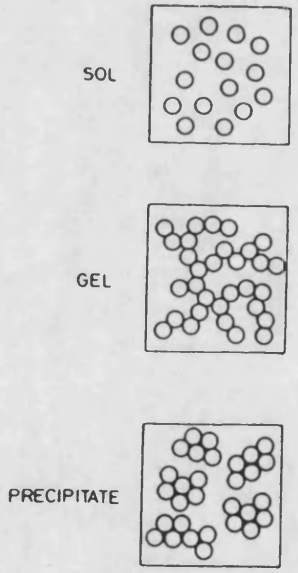


FIGURE 18 - Difference between gelation and precipitation (Zarzycki[1] - 1984)

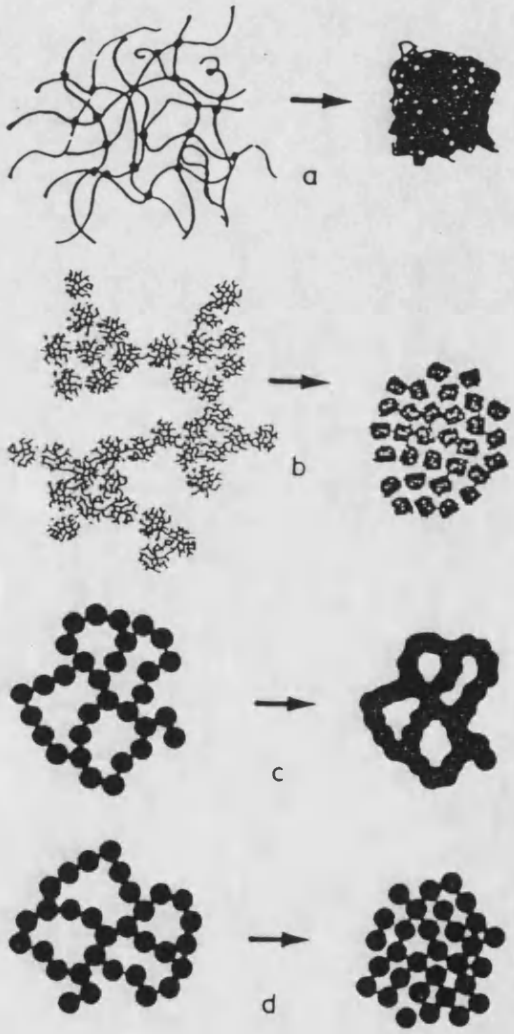
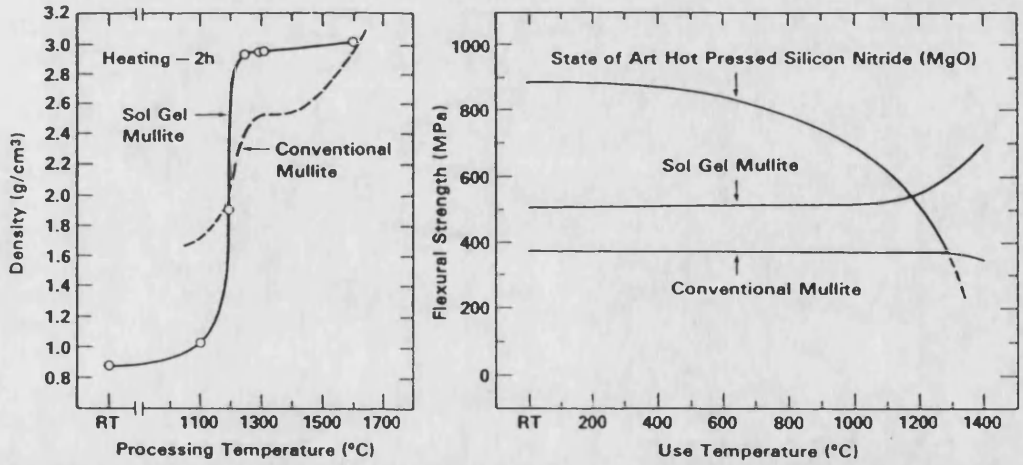


FIGURE 19 - Schematic representation of different gel structures. A. acid catalysed gel; B. base catalysed gel; C. colloidal gel after ageing; D. colloidal gel composed of weakly bonded particles (Scherer - 1988).



- Fully Dense at 1200°C, Not 1600°C
- No Strength Decrease to 1400°C
- Translucent, Not Opaque
- Chemical Uniformity

FIGURE 20 - Comparison of conventional and sol-gel mullite (Ulrich - 1988).

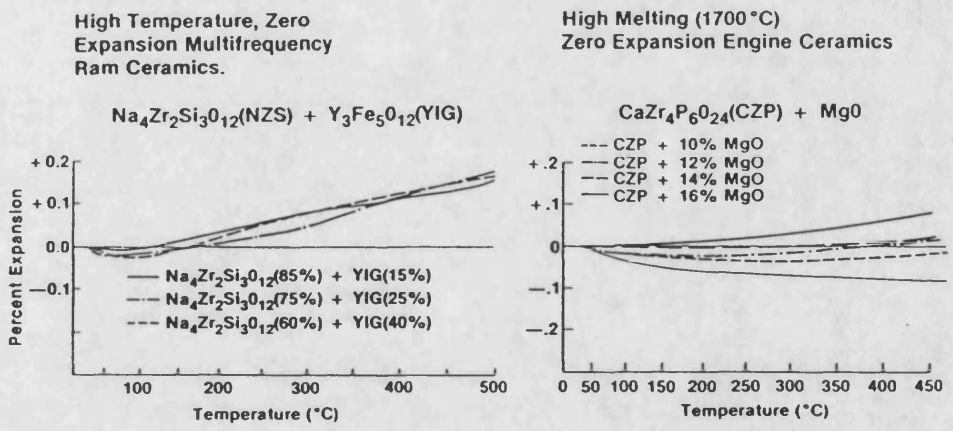


FIGURE 21 - Multifunctional sol-gel nanocomposites; new materials from an ultrastructural composite approach (Ulrich - 1988).

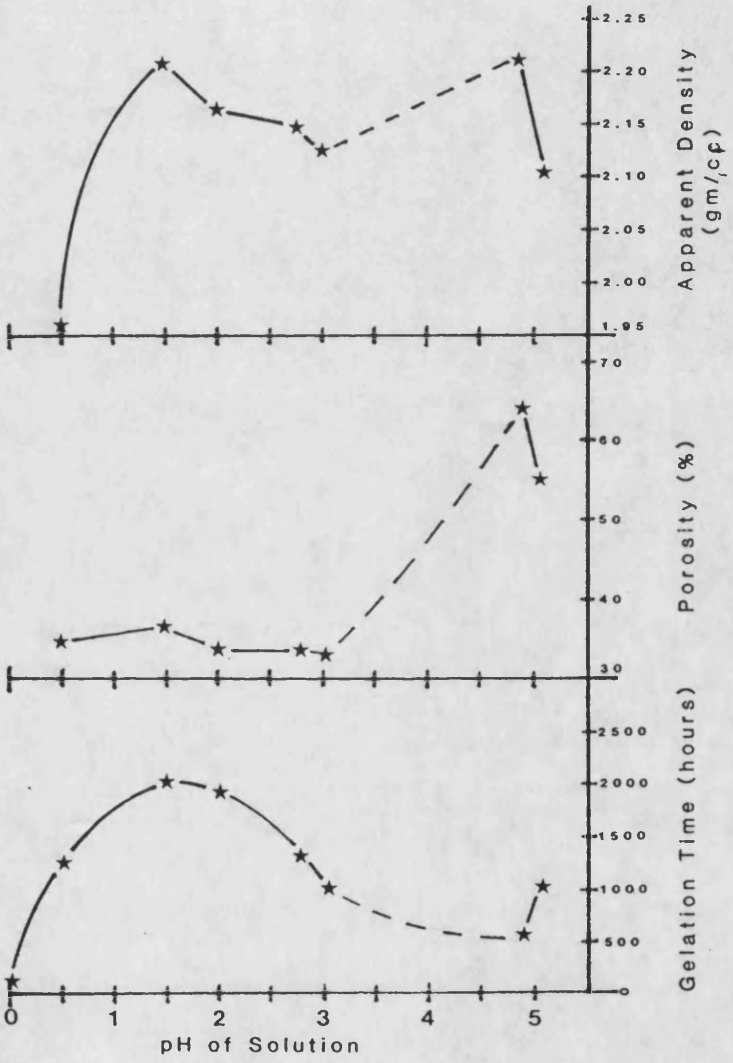


FIGURE 22 - Gelation time, apparent density and porosity as a function of pH for HCl catalyzed solutions (Pope - 1986).

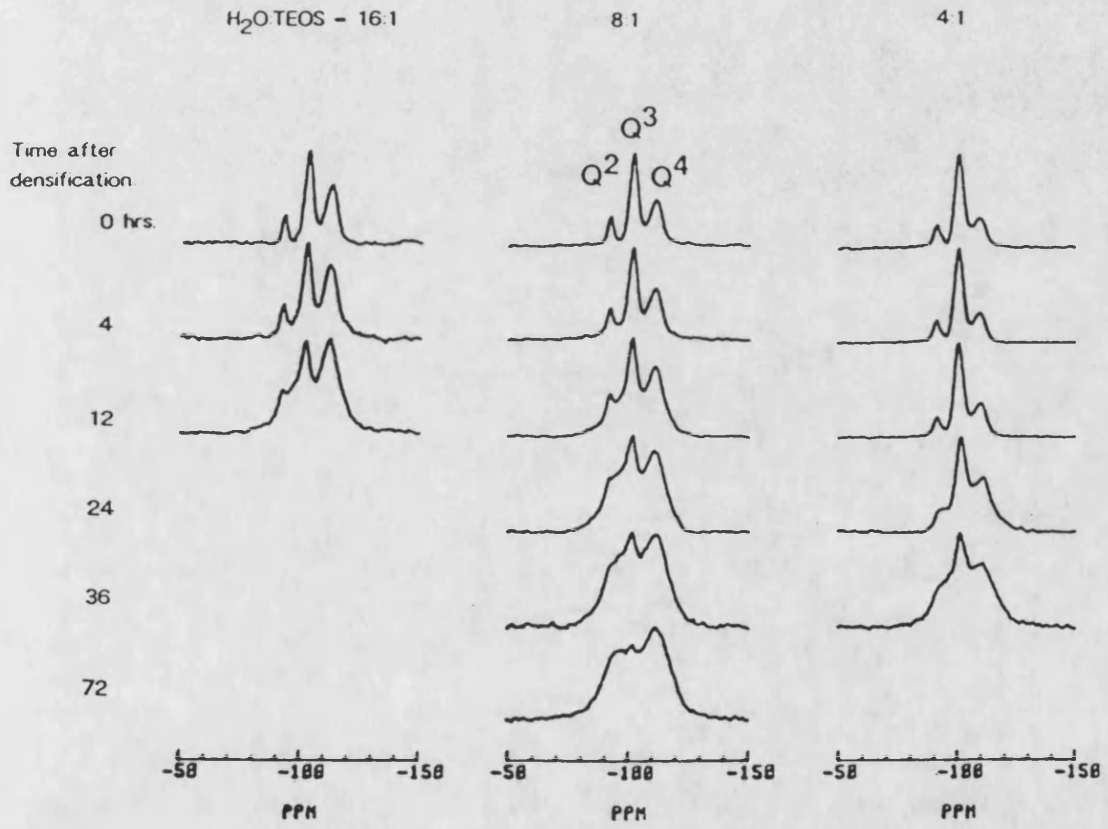


FIGURE 23 - Nonspinning ^{29}Si NMR spectra of silica gels prepared with varying water content - Q^n represents a Si atom bonded through a bridging oxygen to n other Si atoms (Scherer - 1988).

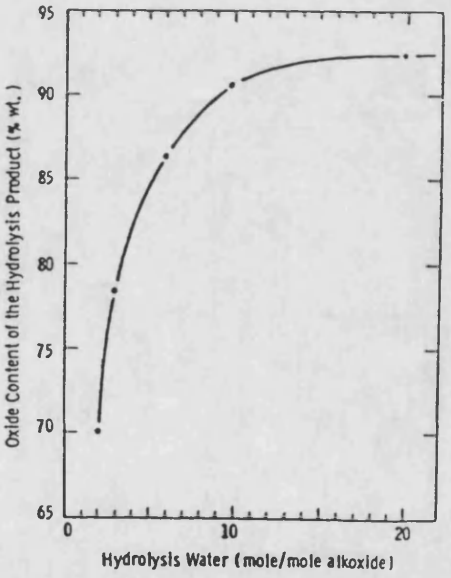


FIGURE 24 - Change in the oxide content of the $Si(OC_2H_5)_4$ hydrolysis product as a function of hydrolysis water (Yoldas - 1982).

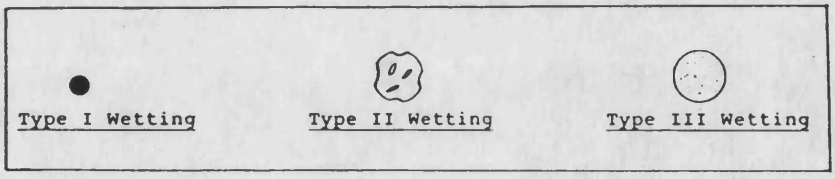


FIGURE 25 - Illustration of a single drop of sol on glass substrate exhibiting type I, II and III wetting (Butts - 1988).

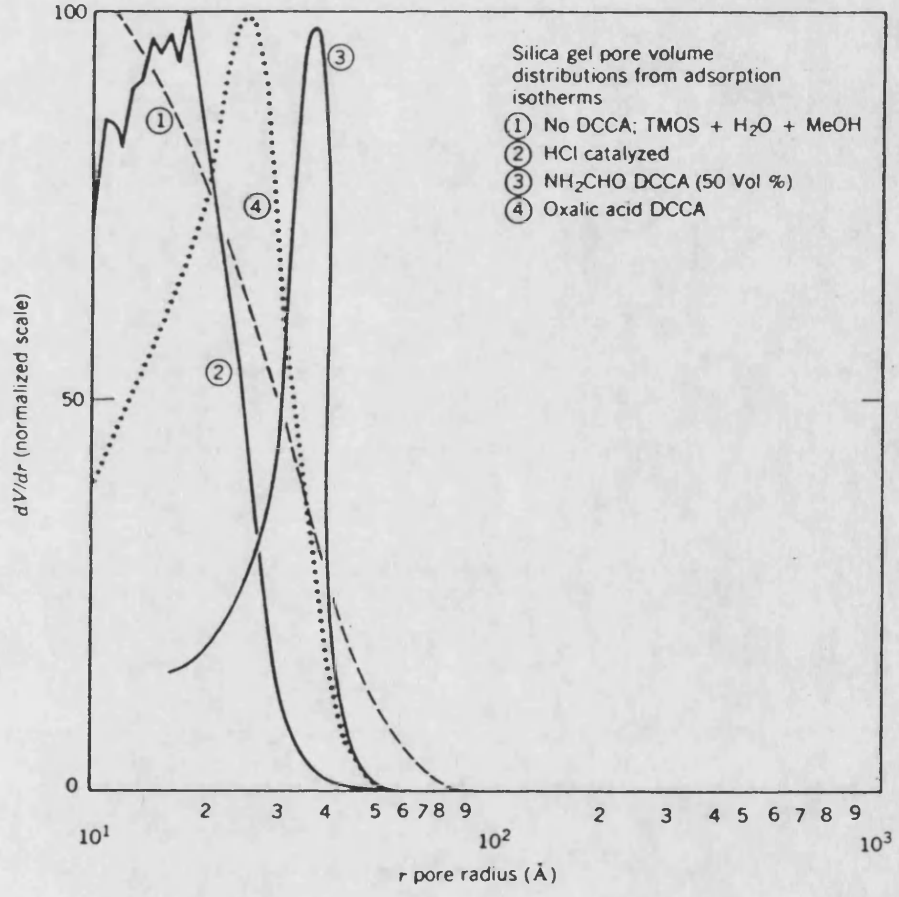


FIGURE 26 - Pore distributions of dried SiO_2 gel monoliths (Hench - 1986).

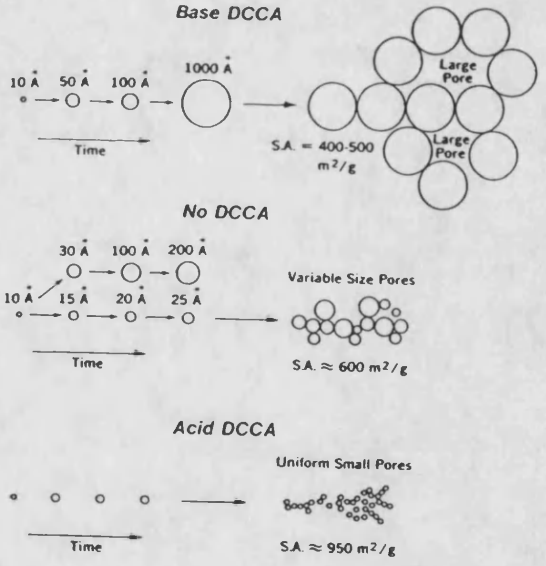


FIGURE 27 - Sol-gel pore size control with DCCAs-sol formation (Ulrich - 1988).

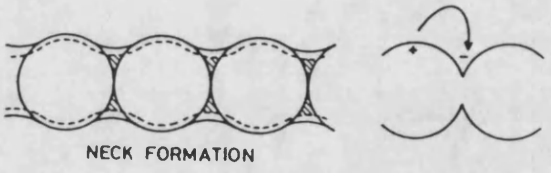


FIGURE 28 - Strengthening of particulate chains by the deposition of silica at the necks (Zarzycki[1] - 1984).

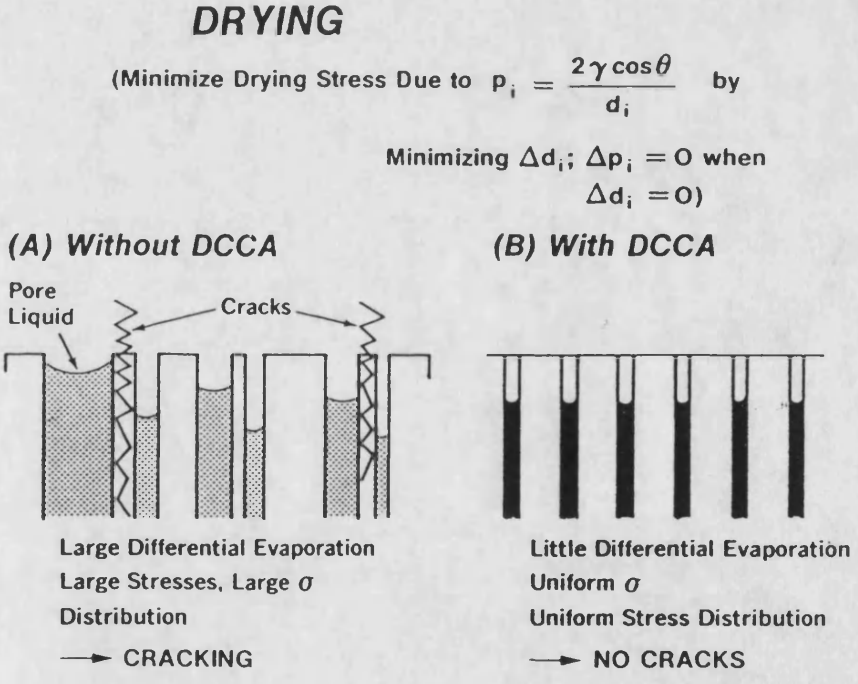


FIGURE 29 - Sol-gel pore size control with DCCAs-drying (Ulrich - 1988).

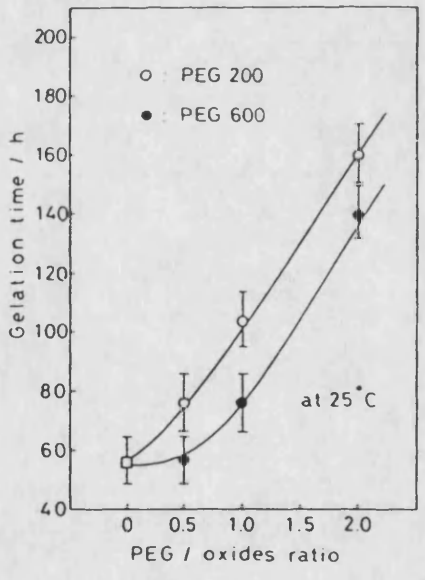


FIGURE 30 - Gelation time against the wt ratio of PEG to equivalent oxides ($20B_2O_3.80SiO_2$) (Tohge - 1988).

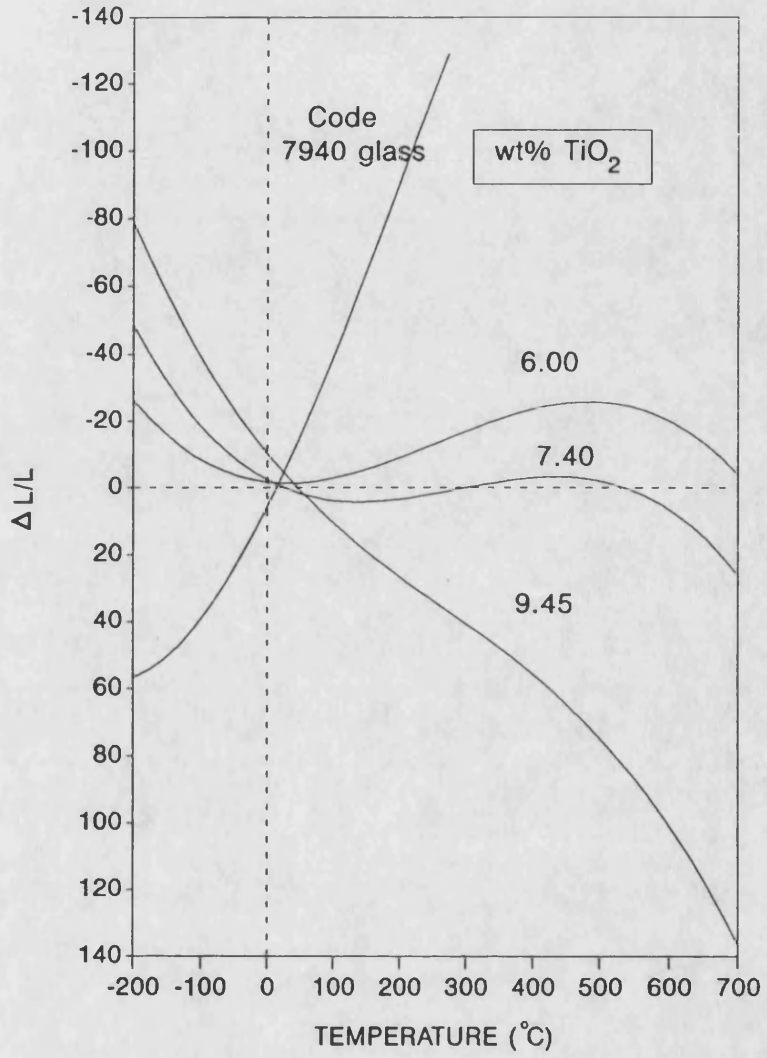


FIGURE 31 - Thermal expansion of annealed vitreous silica and SiO_2-TiO_2 glasses (Lewis - 1971).

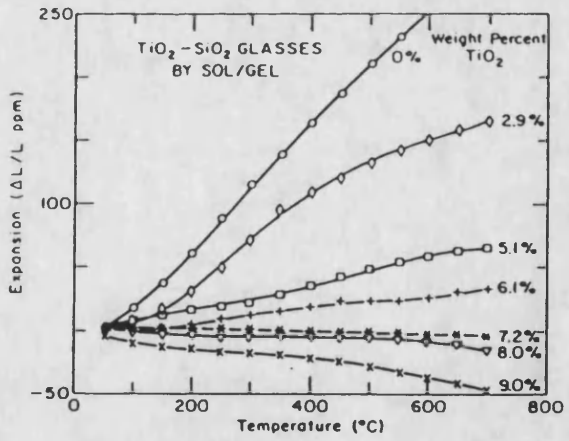


FIGURE 32 - Thermal expansion curves for titania-silica glasses prepared by the colloidal sol/gel method; obtained using differential dilatometer with Corning's 7971 for reference (Deng - 1988).

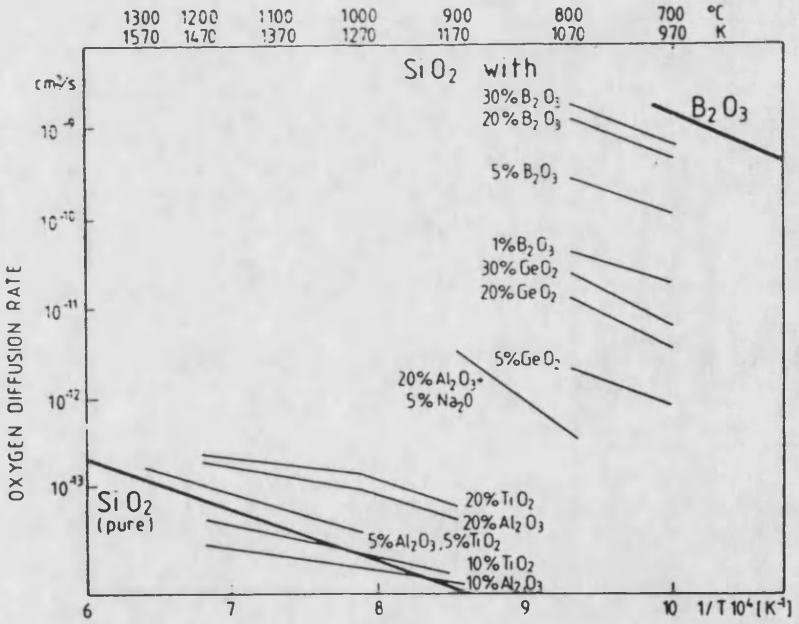


FIGURE 33 - Temperature dependence of calculated oxygen diffusion coefficients for different glasses (Schlichting - 1984).

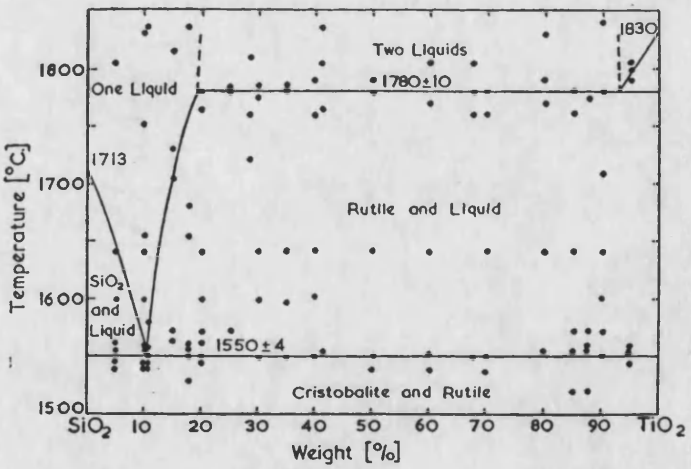


FIGURE 34 - Proposed phase equilibrium diagram for the system TiO_2-SiO_2 (DeVries - 1954).

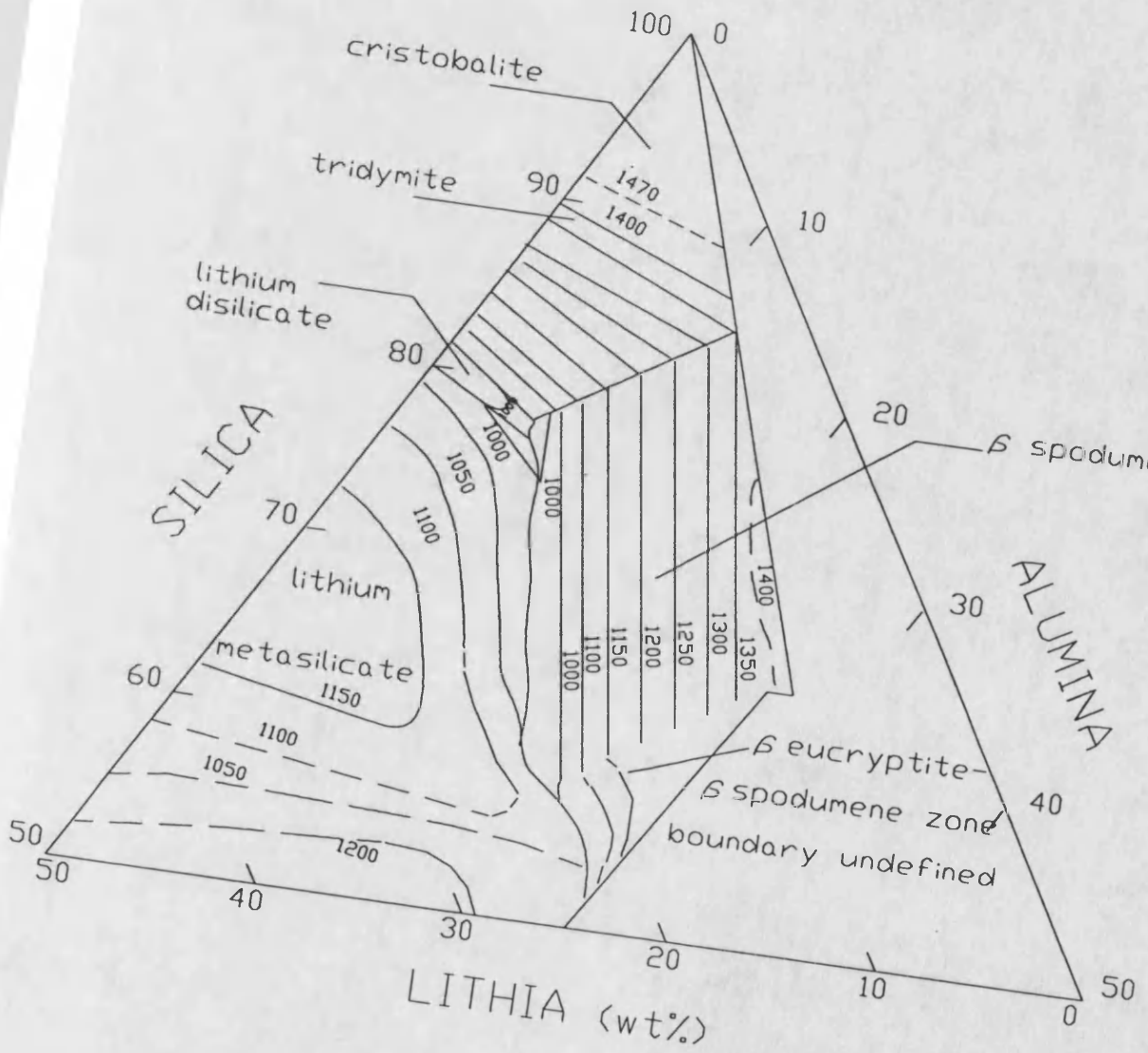


FIGURE 35 - The system lithia-alumina-silica showing proposed liquidus relations (Eppler - 1963).

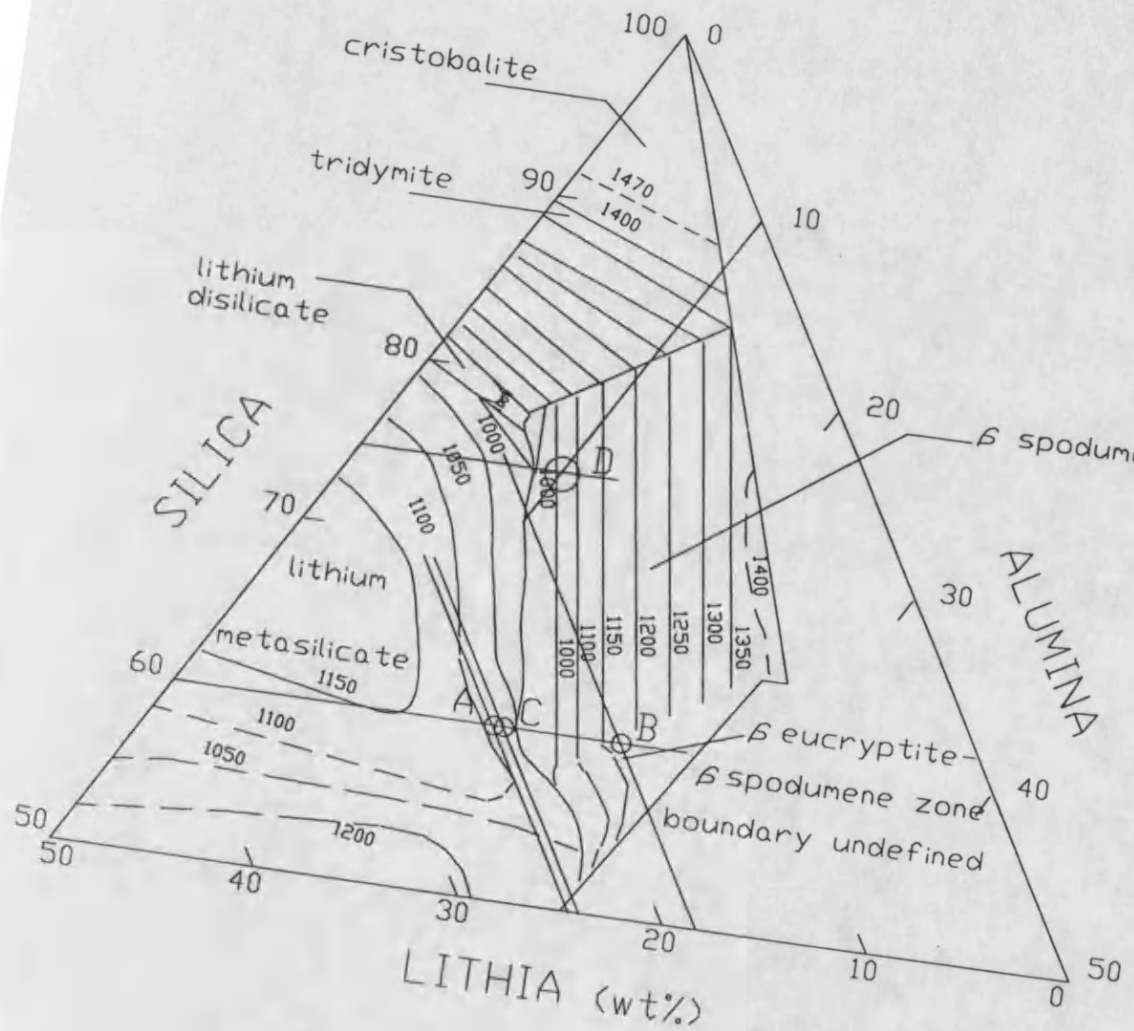
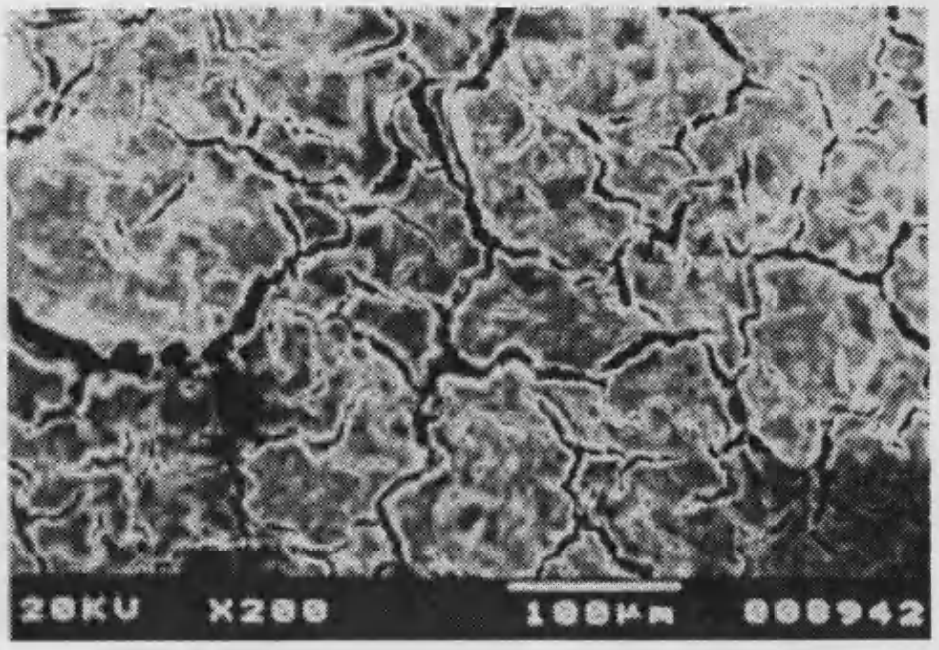


FIGURE 36 - Composition of lithium aluminium silicates. A, B and D produced by Corning (Corning Glass Works - 1970); C composition selected for this work.



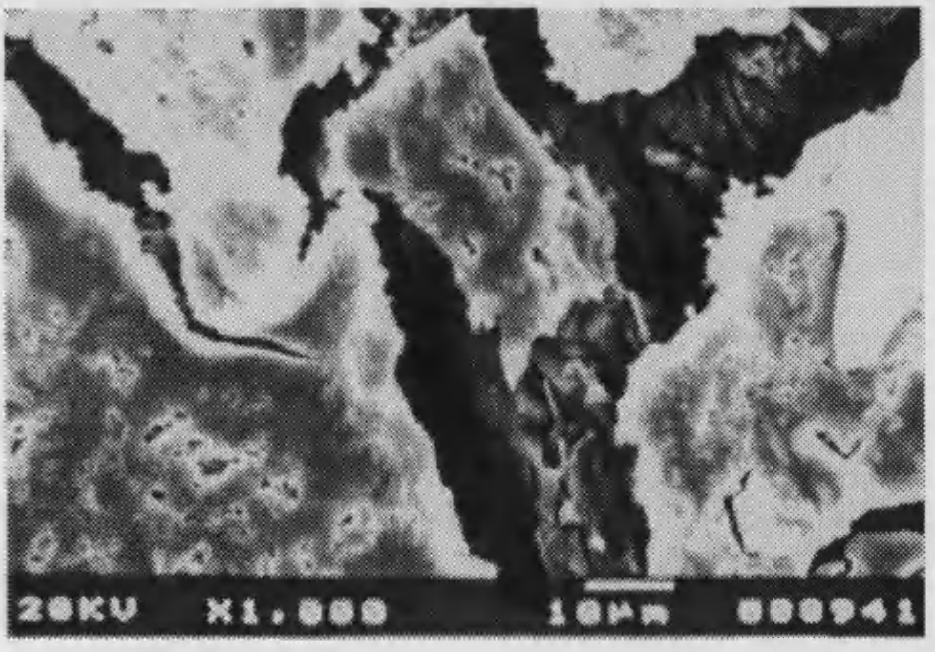
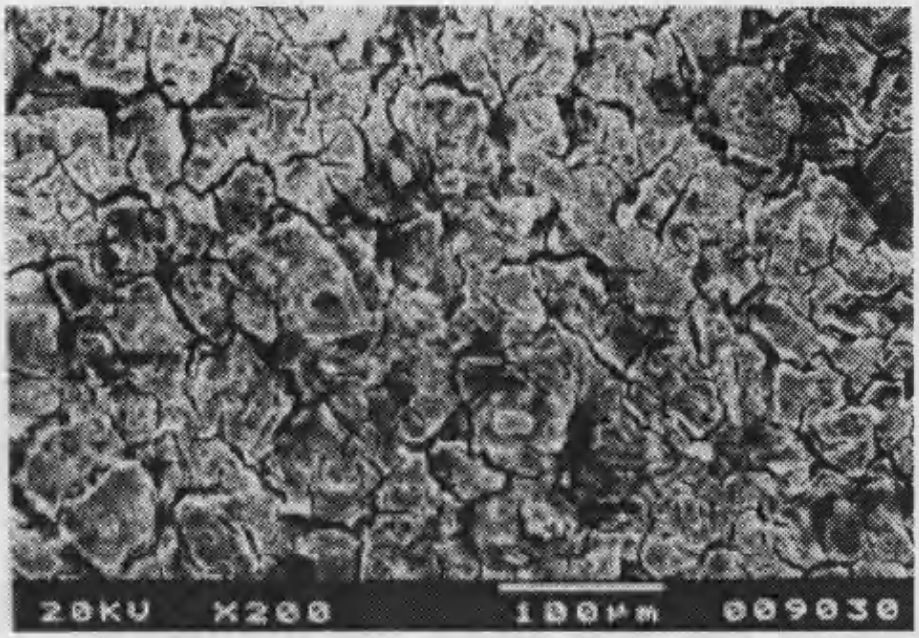


FIGURE 37 - Mosaic texture of the gel 56 produced using 8 mol water/mol TEOS, ethanol (solvent) and no additive (glycerol), dried but not fired. A - X200, B - X1000.



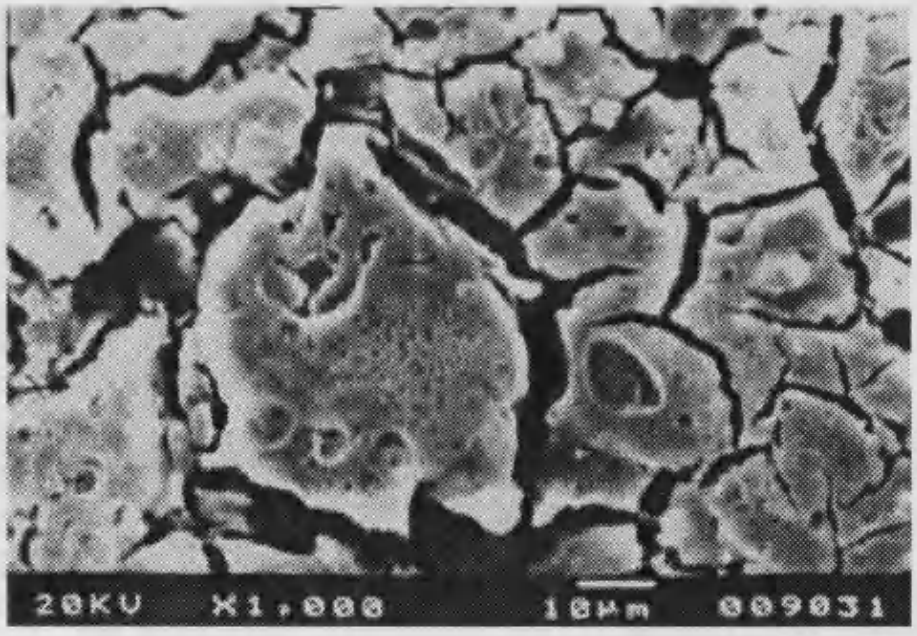
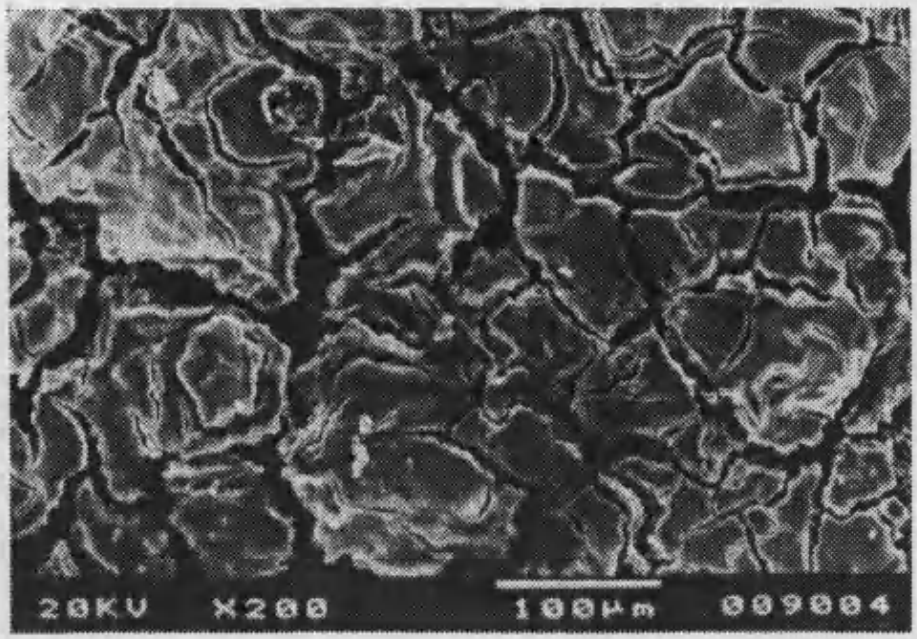


FIGURE 38 - Mosaic texture of the gel 80 produced using 16 mol water/mol TEOS, ethanol (solvent) and no additive (glycerol), dried but not fired. A - X200, B - X1000.



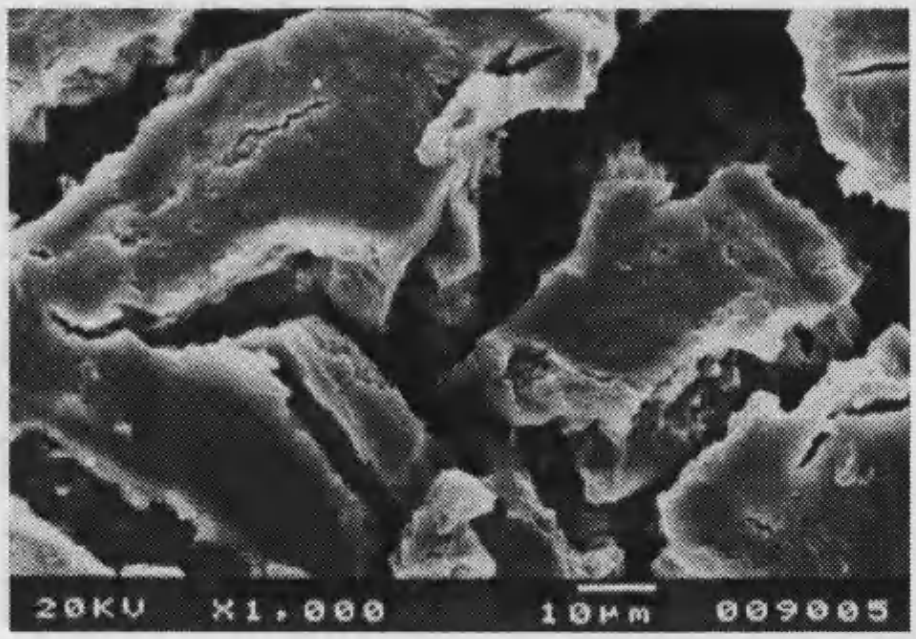
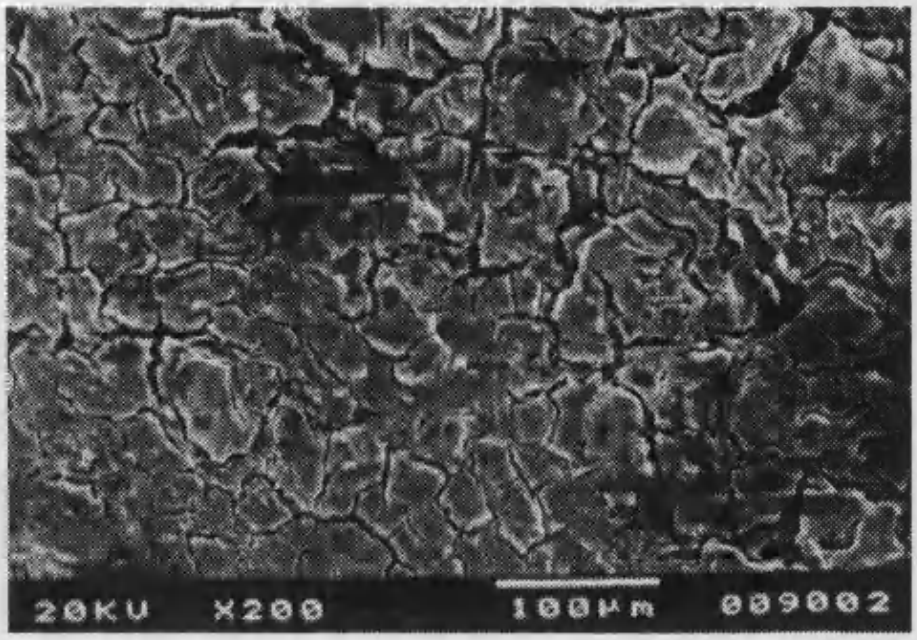


FIGURE 39 - Mosaic texture of the gel 68 produced using 8 mol water/mol TEOS, propanol (solvent) and no additive (glycerol), dried but not fired. A - X200, B - X1000.



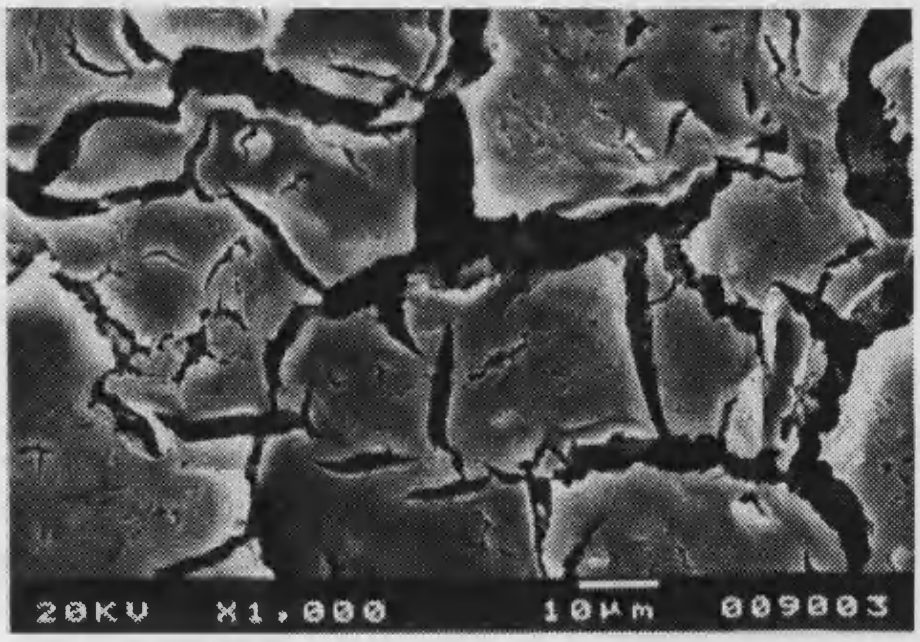
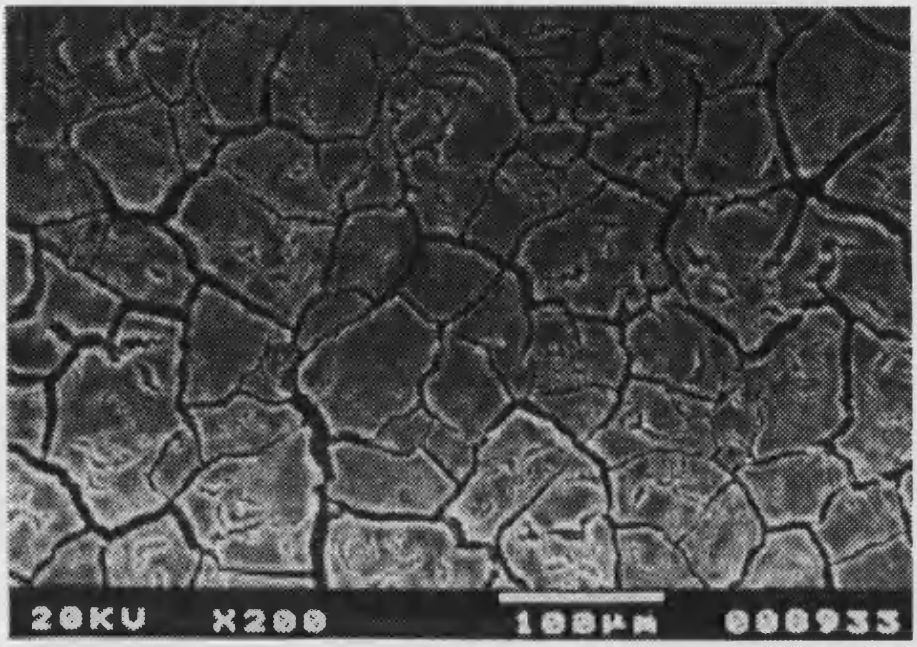


FIGURE 40 - Mosaic texture of the gel 92 produced using 16 mol water/mol TEOS, propanol (solvent) and no additive (glycerol), dried but not fired. A - X200, B - X1000.



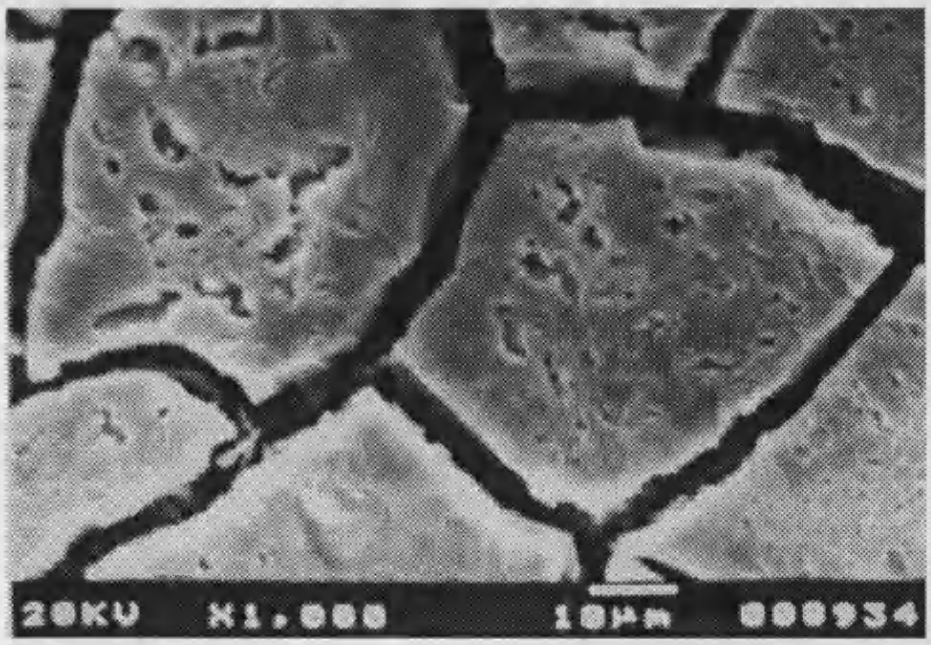
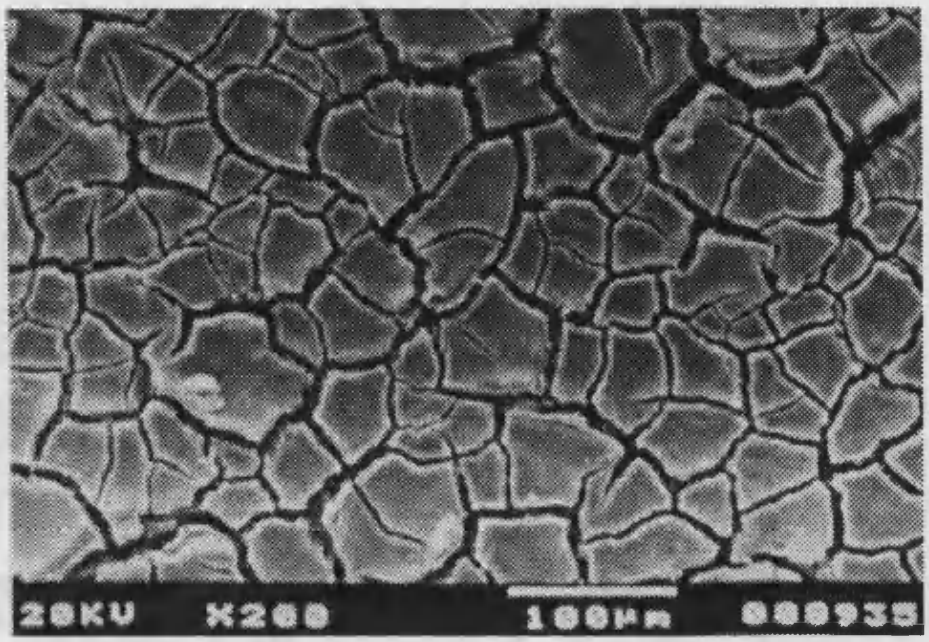


FIGURE 41 - Mosaic texture of the gel 52 produced using 8 mol water/mol TEOS, ethanol (solvent) and glycerol, dried but not fired. A - X200, B - X1000.



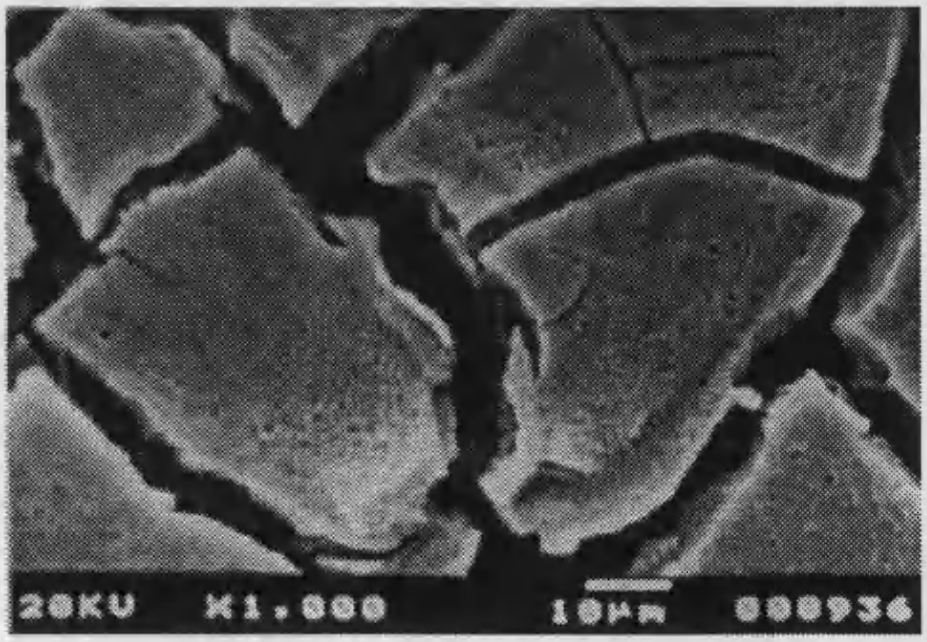
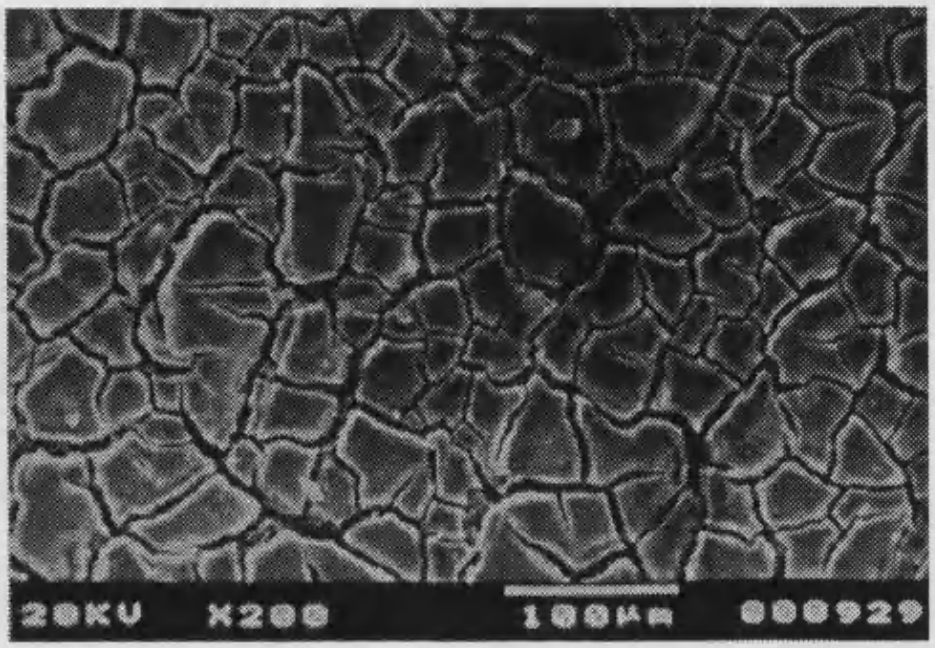


FIGURE 42 - Mosaic texture of the gel 77 produced using 16 mol water/mol TEOS, ethanol (solvent) and glycerol, dried but not fired. A - X200, B - X1000.



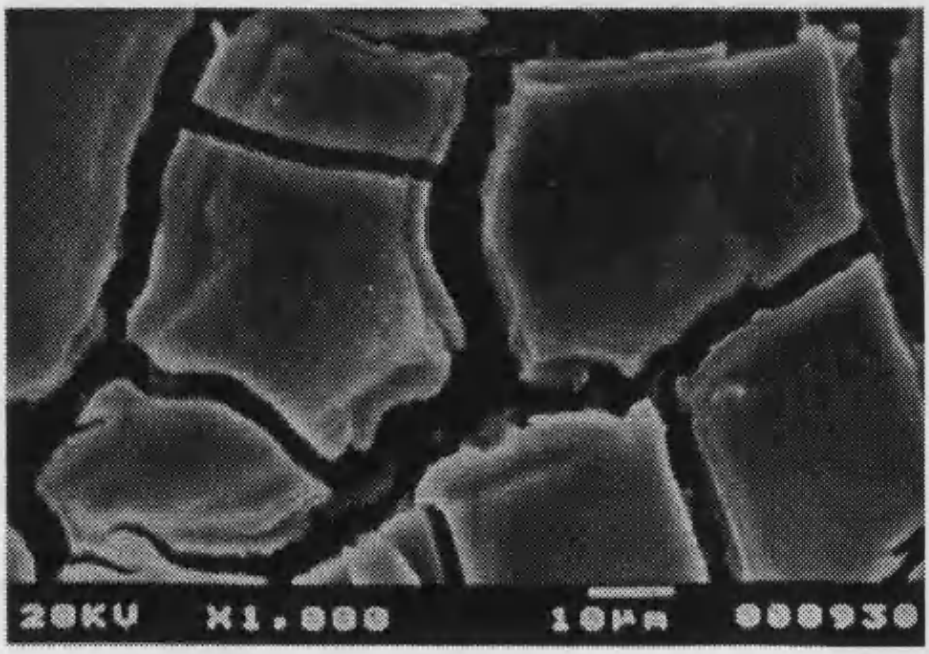


FIGURE 43 - Mosaic texture of the gel 65 produced using 8 mol water/mol TEOS, propanol (solvent) and glycerol, dried but not fired. A - X200, B - X1000

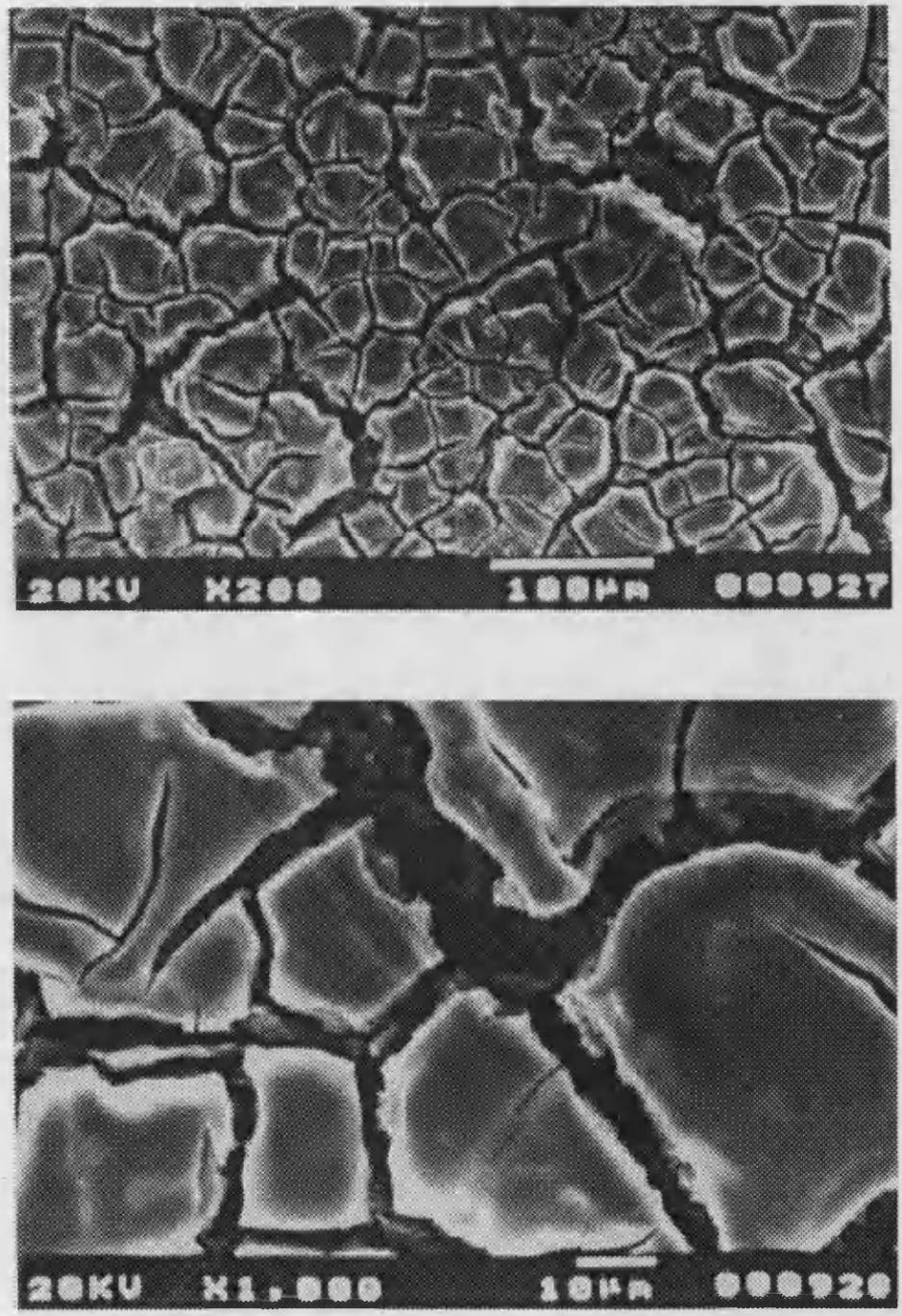


FIGURE 44 - Mosaic texture of the gel 89 produced using 16 mol water/mol TEOS, propanol (solvent) and glycerol, dried but not fired. A - X200, B - X1000

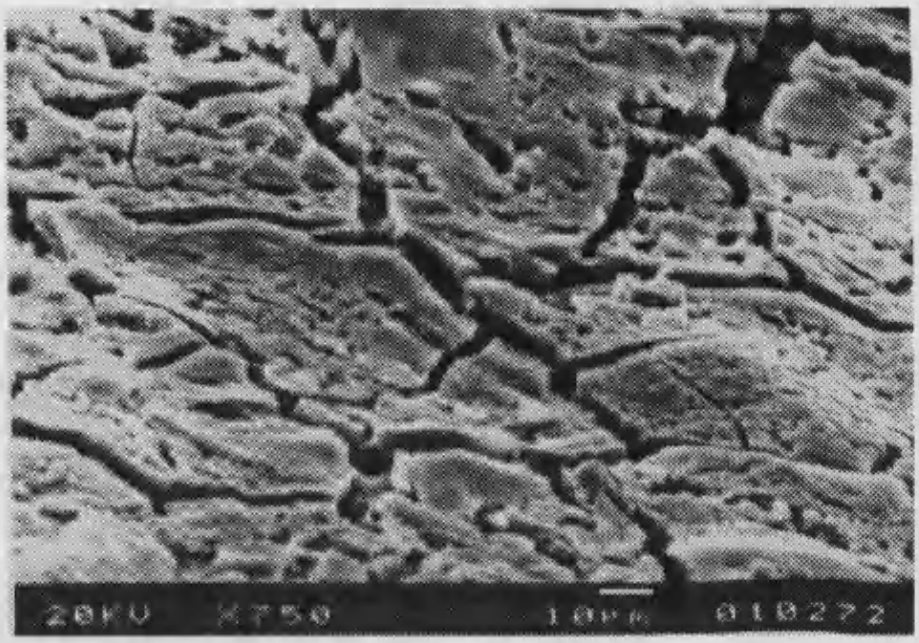


FIGURE 45 - Mosaic texture of single layer gel coating after drying exhibiting large internal defects and flat particles.

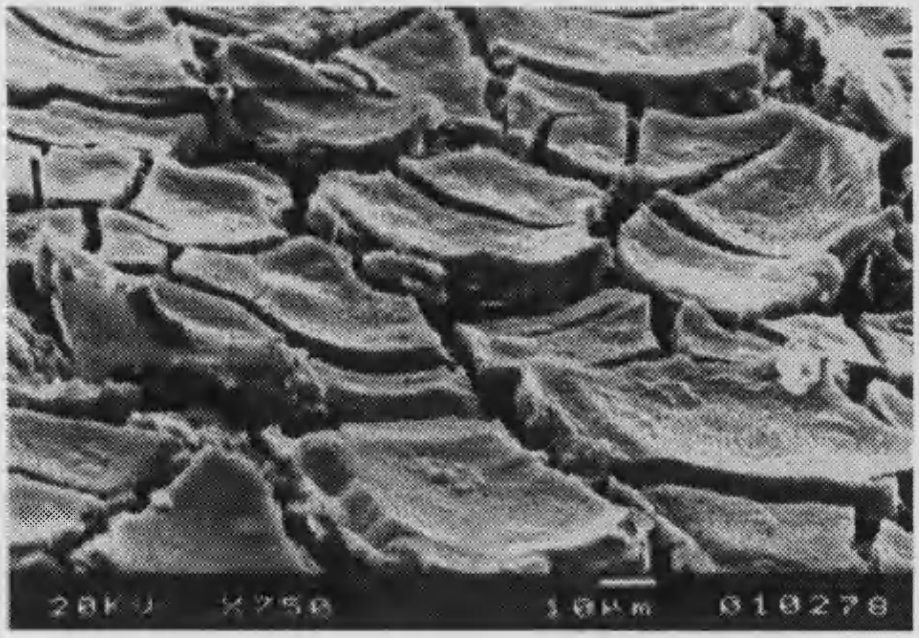


FIGURE 46 - Mosaic texture of single layer gel coating after drying exhibiting small internal defects and slightly bent particles.

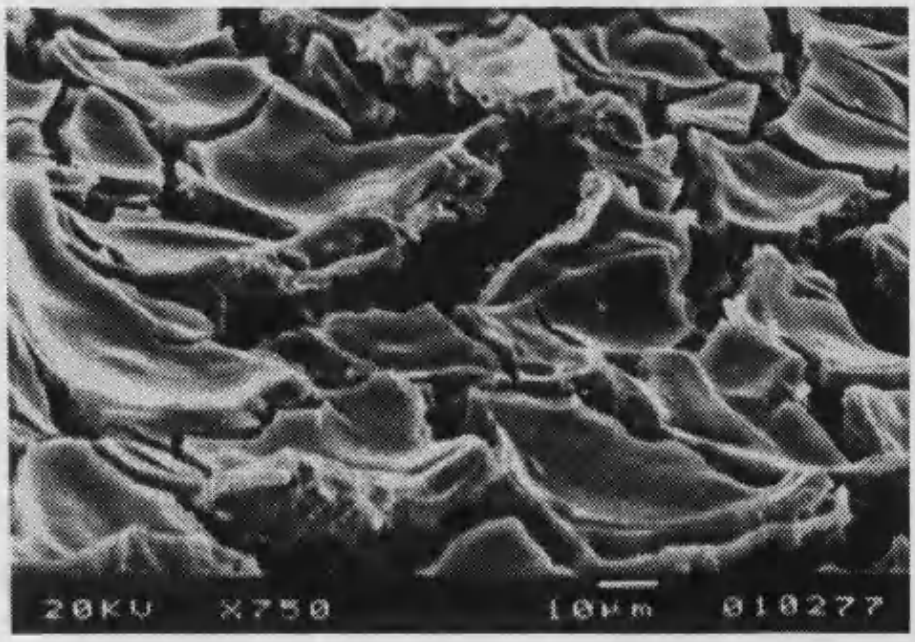


FIGURE 47 - Mosaic texture of single layer gel coating after drying exhibiting no internal defects and severely bent particles.

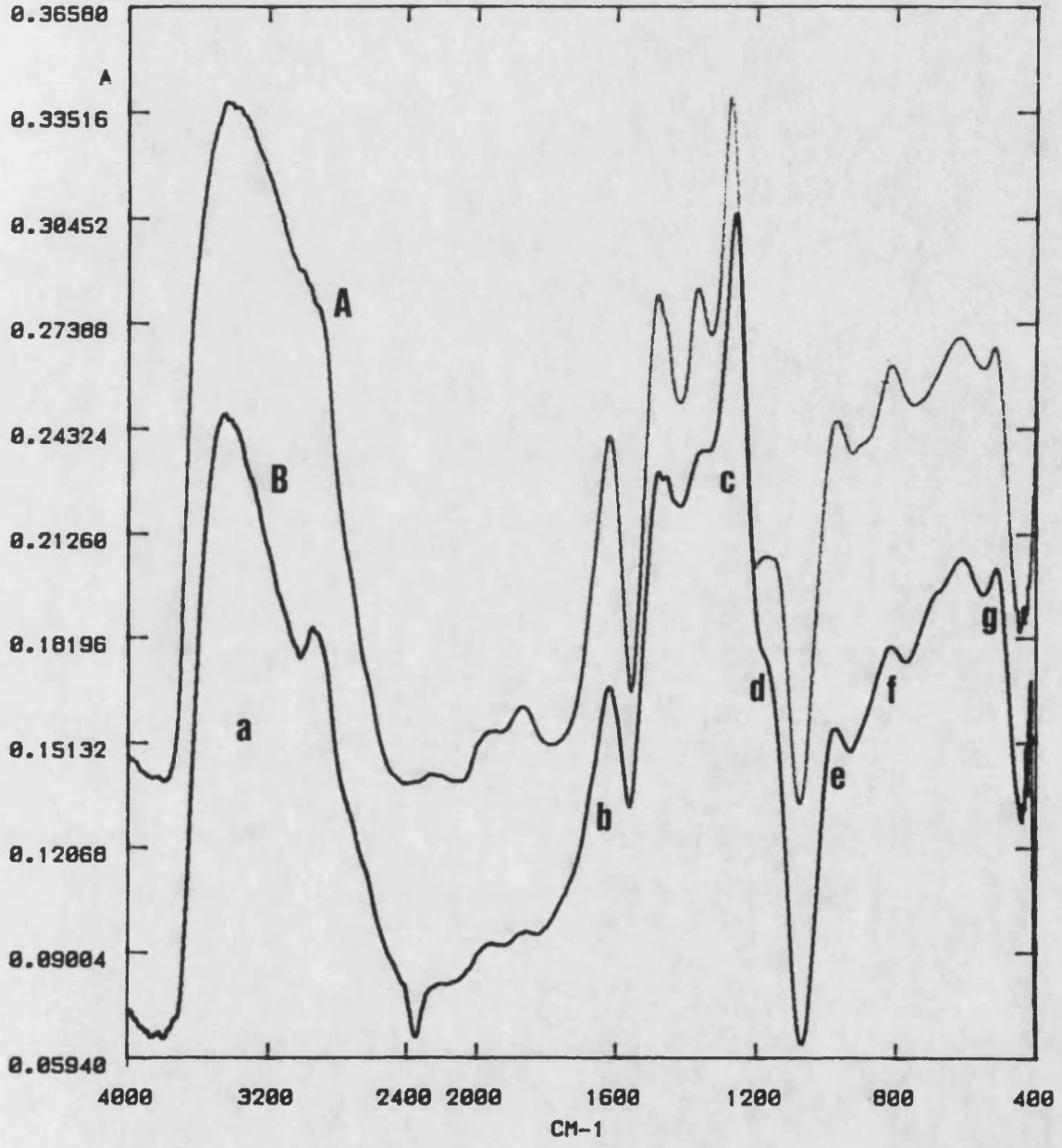


FIGURE 48 - FT-IR diffusive reflectance spectra for the dried gels (60°C - 24 h). A - gel 56 produced using ethanol and no glycerol; B - gel 52 produced using ethanol and glycerol.

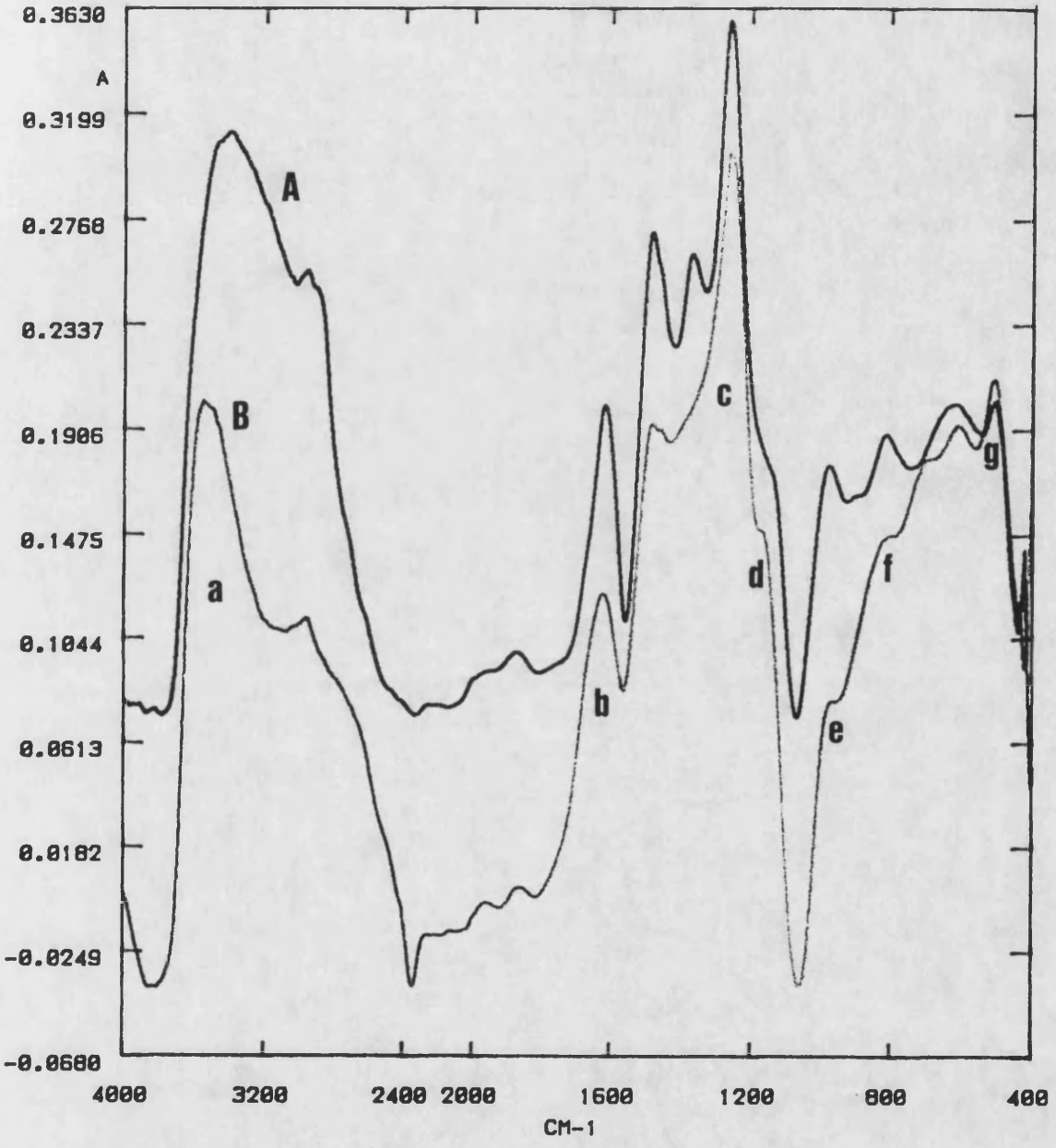


FIGURE 49 - FT-IR diffusive reflectance spectra for the dried gels (60°C - 24 h). A - gel 68 produced using propanol and no glycerol; B - gel 65 produced using propanol and glycerol.

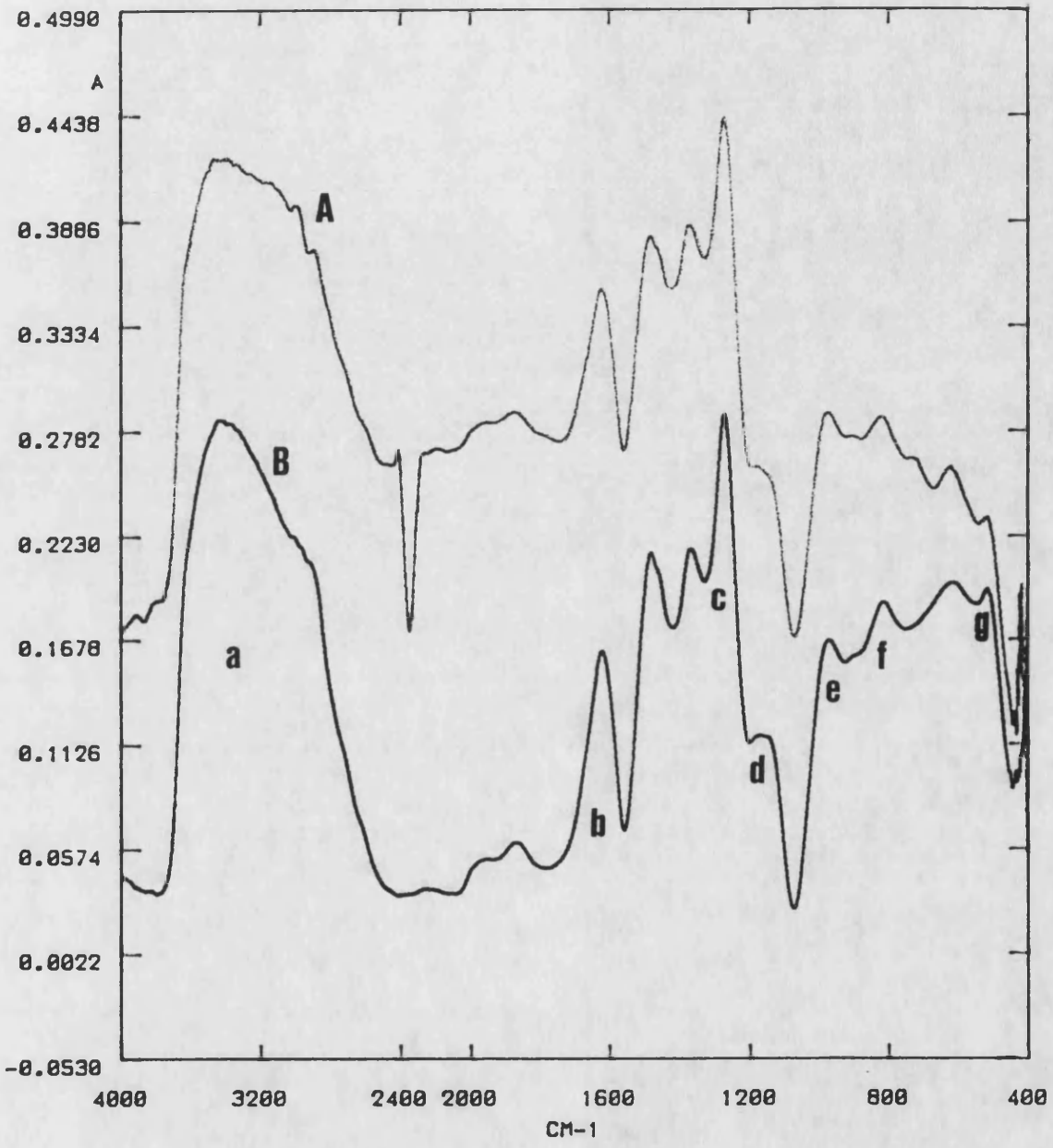


FIGURE 50 - FT-IR diffusive reflectance spectra for the gel 56 produced using ethanol and no glycerol:A-56 wet; B-56 dried (60°C-24 h).

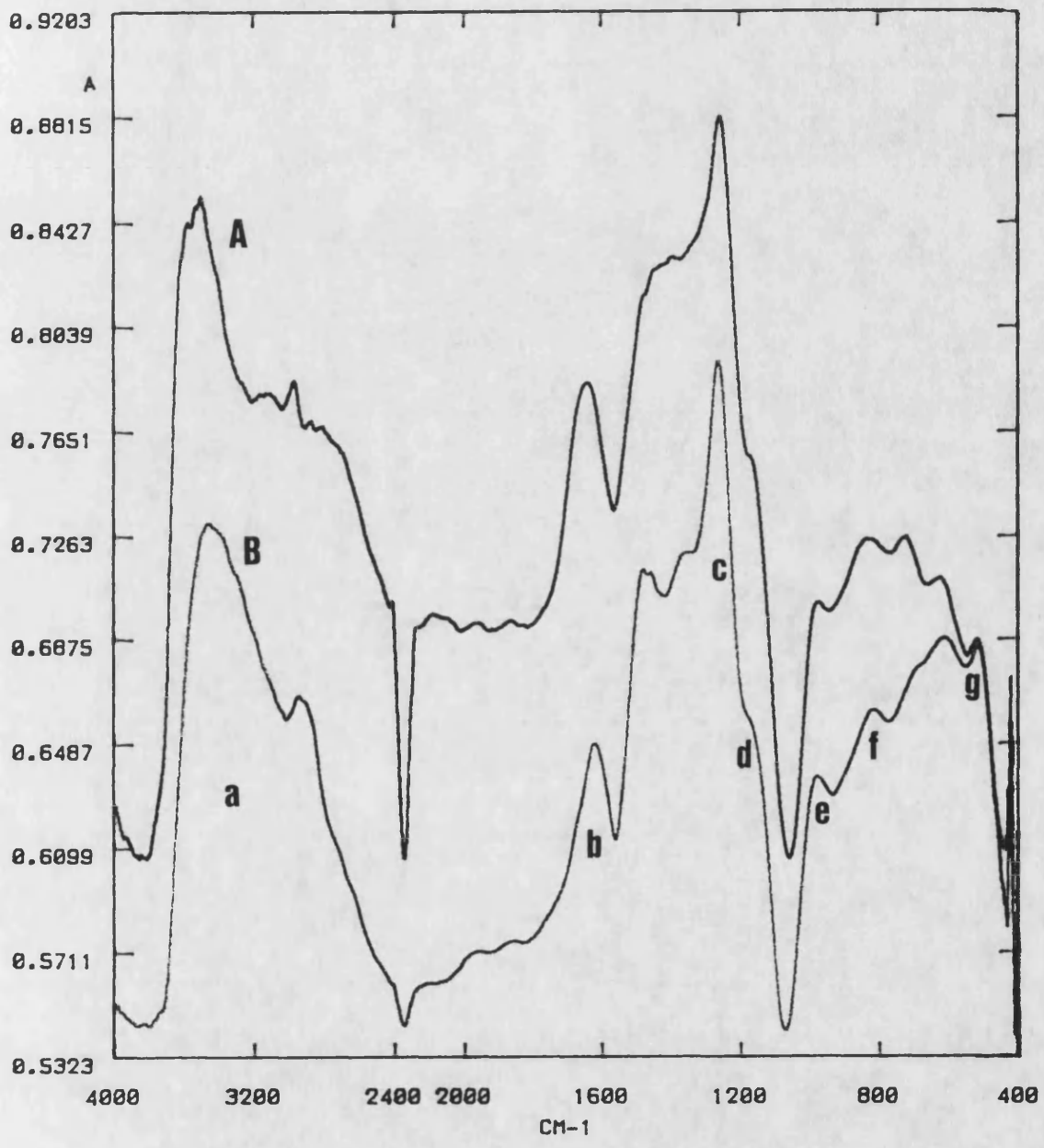


FIGURE 51 - FT-IR diffusive reflectance spectra for the gel 52 produced using ethanol and glycerol: A-52 wet; B-52 dried (60°C - 24 h).

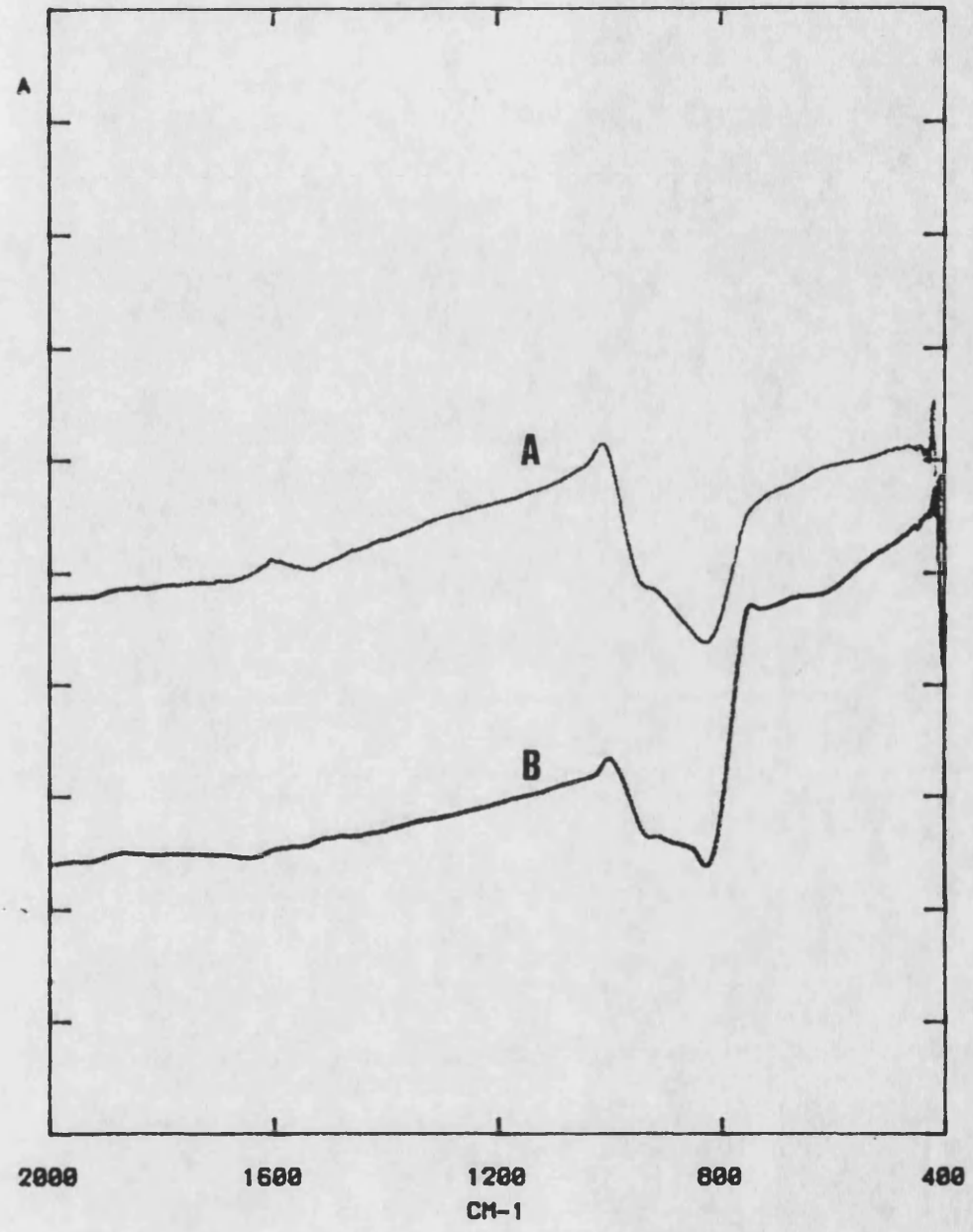


FIGURE 52 - FT-IR diffusive reflectance spectra for the SiC particles supplied by Carborundum (A) and for the SiC coating produced from gel 56(B).

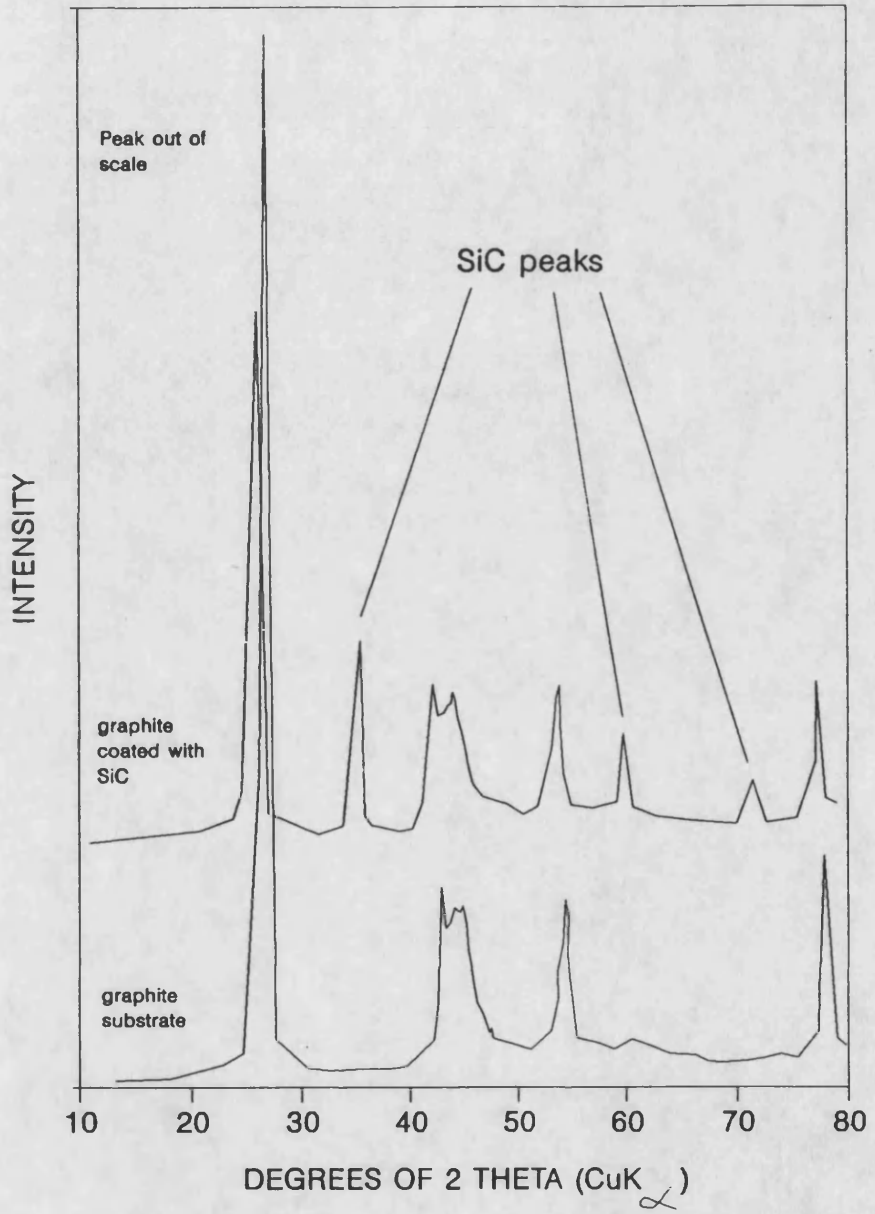


FIGURE 53 - X-Ray diffraction analysis for the uncoated and coated graphite sample showing conclusively the formation of SiC.

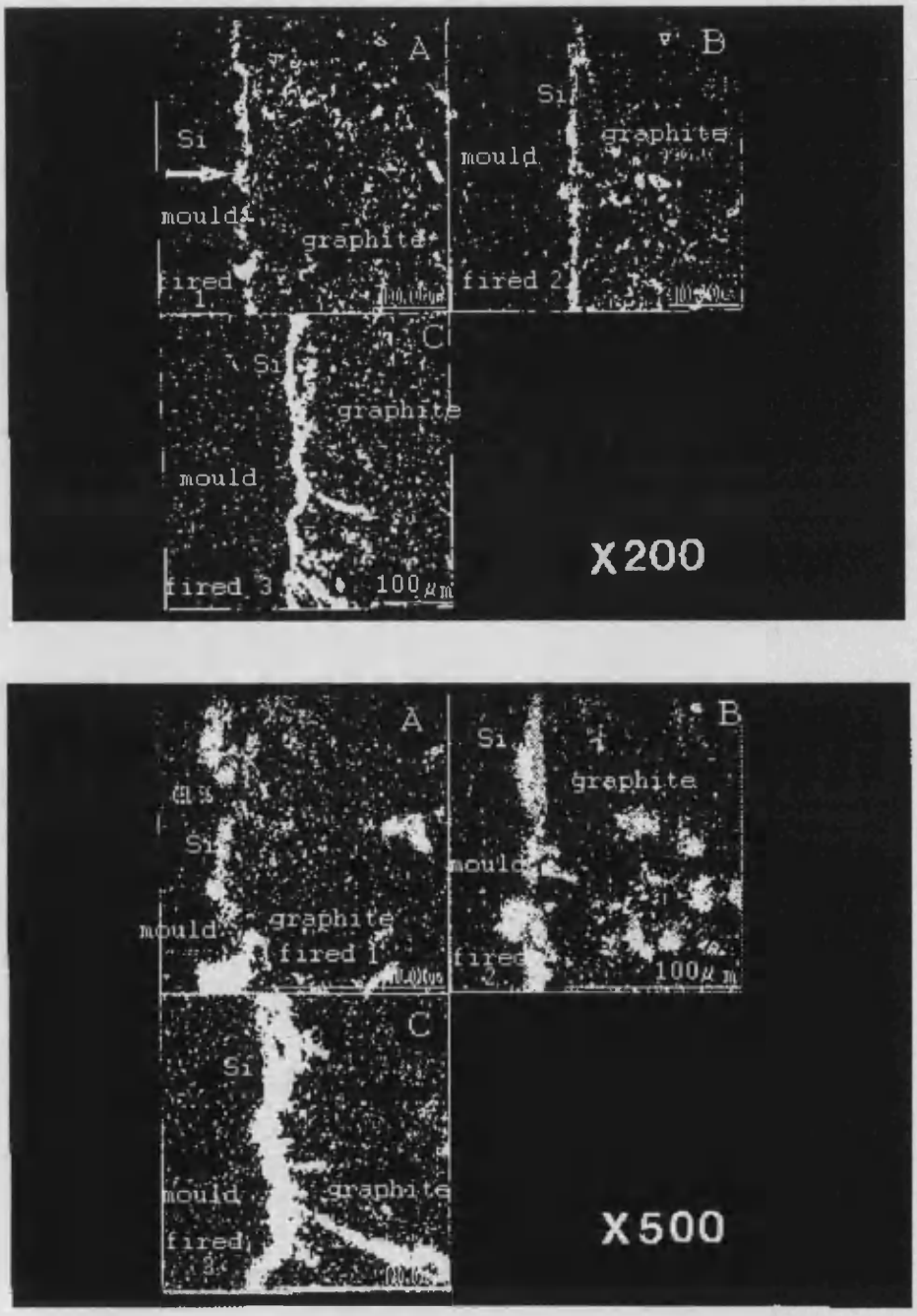


FIGURE 54 - X-Ray image for Si on electrode graphite. A. fired once; B. fired twice; C. fired three times.

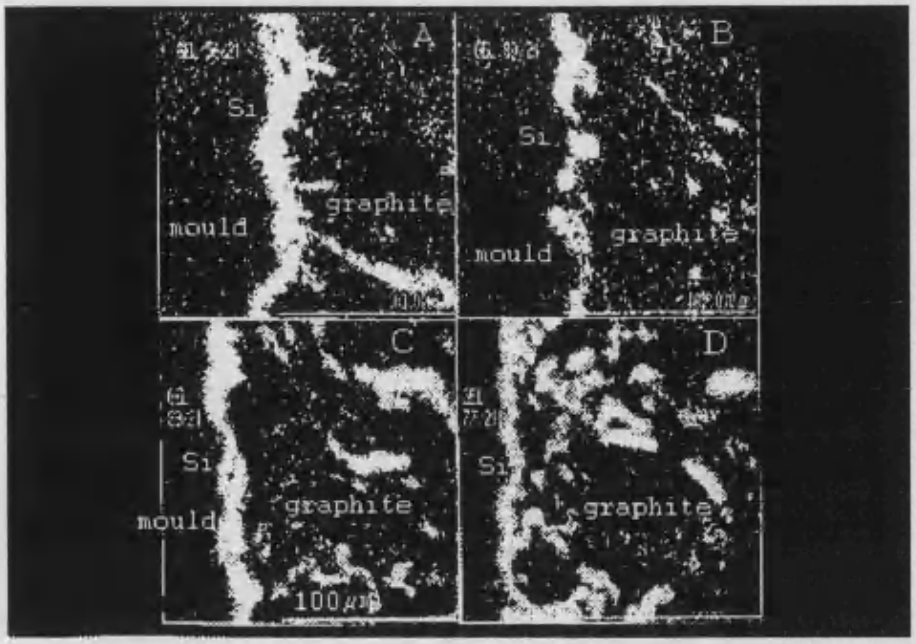


FIGURE 55 - X-Ray image for Si on electrode graphite (X500) produced by different gels. A. gel 56; B. gel 80; C. gel 89; D. gel 77.

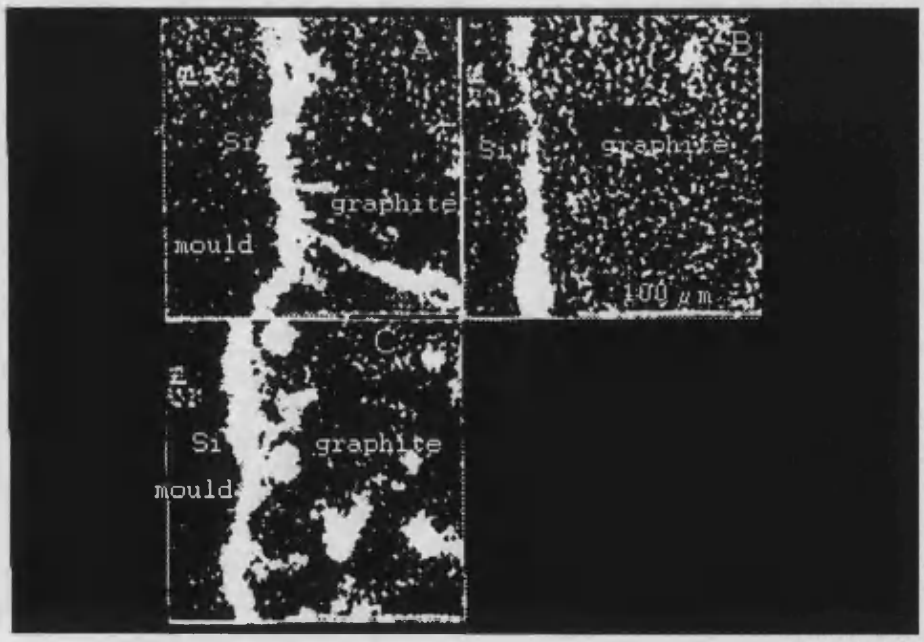


FIGURE 56 - X-Ray image for Si on electrode graphite (X500) produced by different gels. A. gel 56; B. gel 32; C. gel 92.

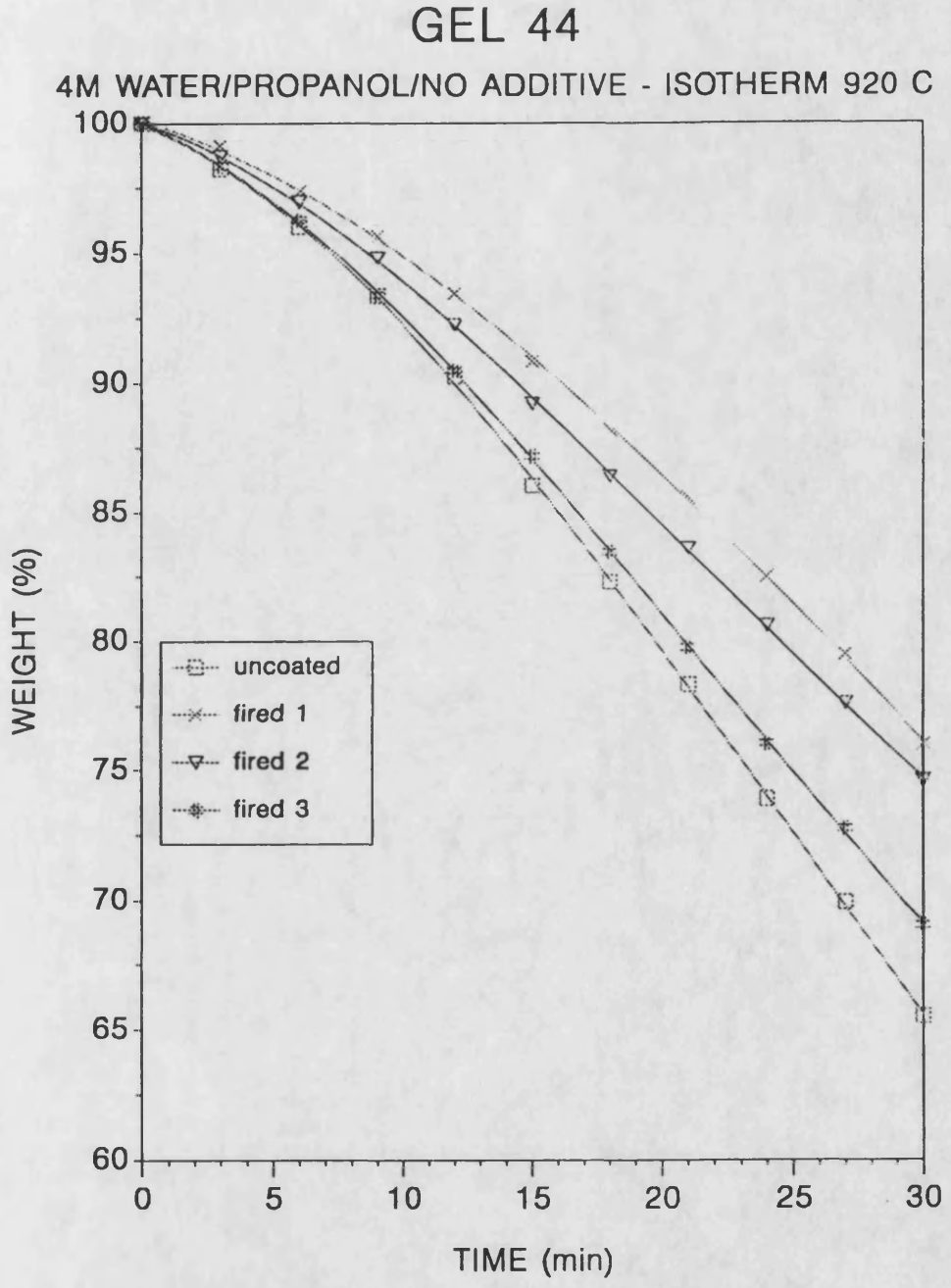


FIGURE 57 - Comparative TGA results for the samples coated with the gel 44 (4 moles of water/mol of TEOS, using propanol, and no glycerol) fired once, twice and three times.

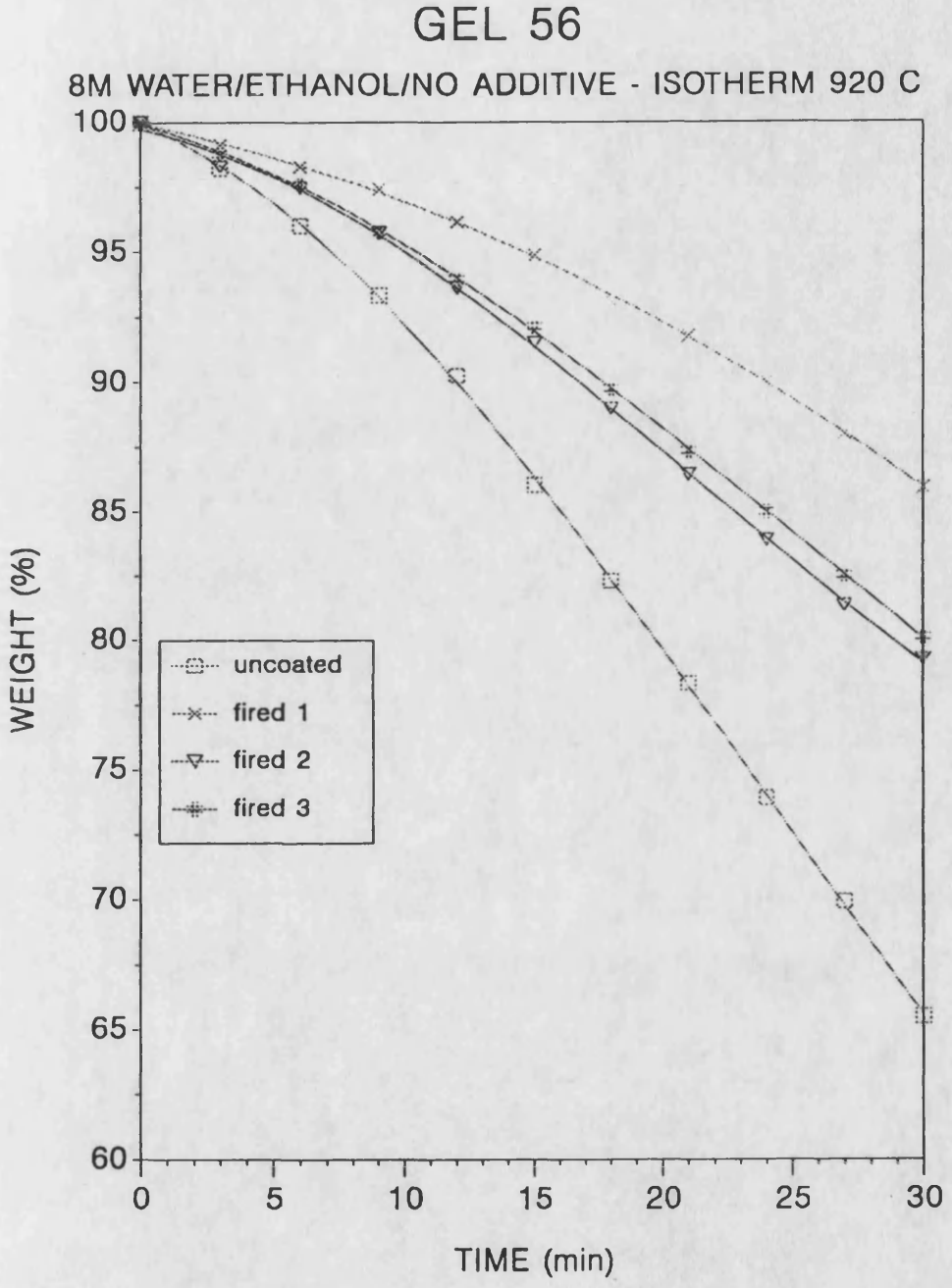


FIGURE 58 - Comparative TGA results for the samples coated with the gel 56 (8 moles of water/mol of TEOS, using ethanol, and no glycerol) fired once, twice and three times.

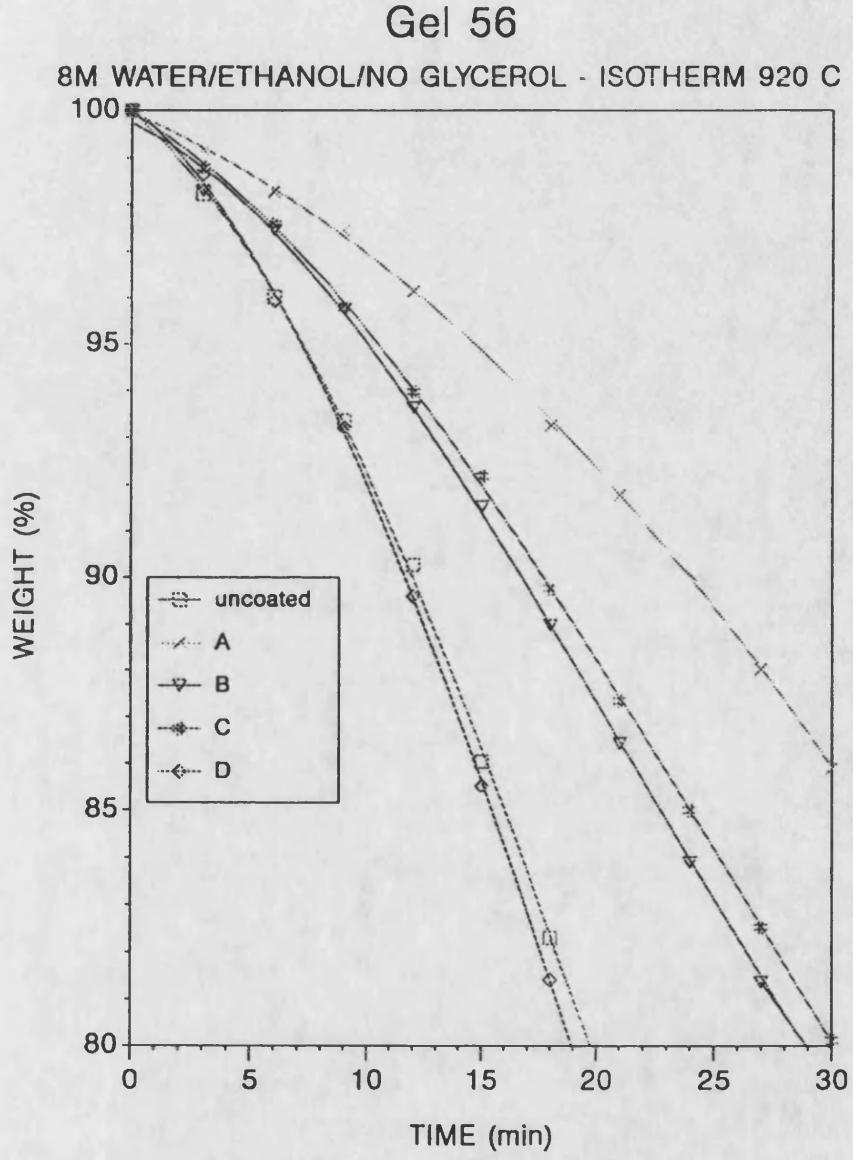


FIGURE 59 - Comparative TGA results for samples coated and fired once (A), coated and fired twice (B), coated and fired three times (A), and coated once and fired twice (D).

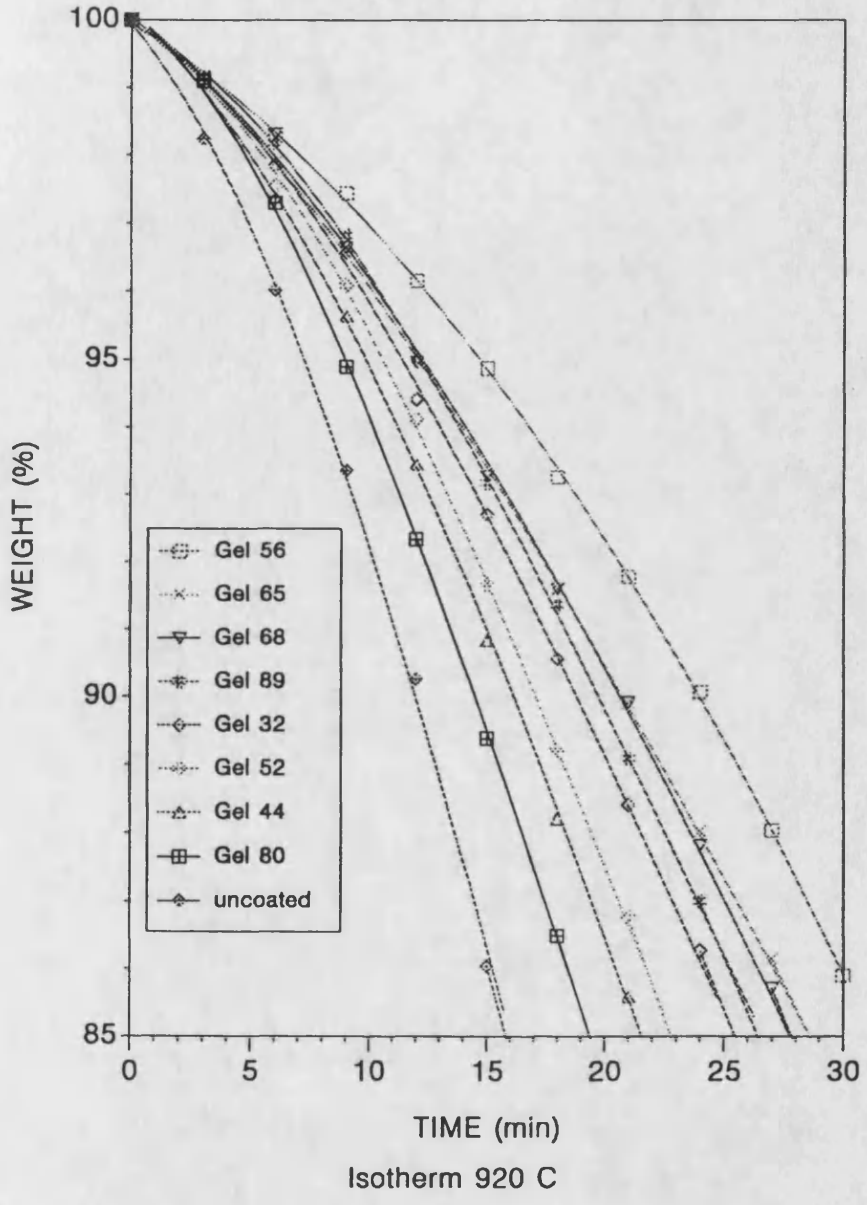


FIGURE 60 - Comparative TGA results for electrode graphite samples fired once. Selection of the 8 best gels among the 10 studied.

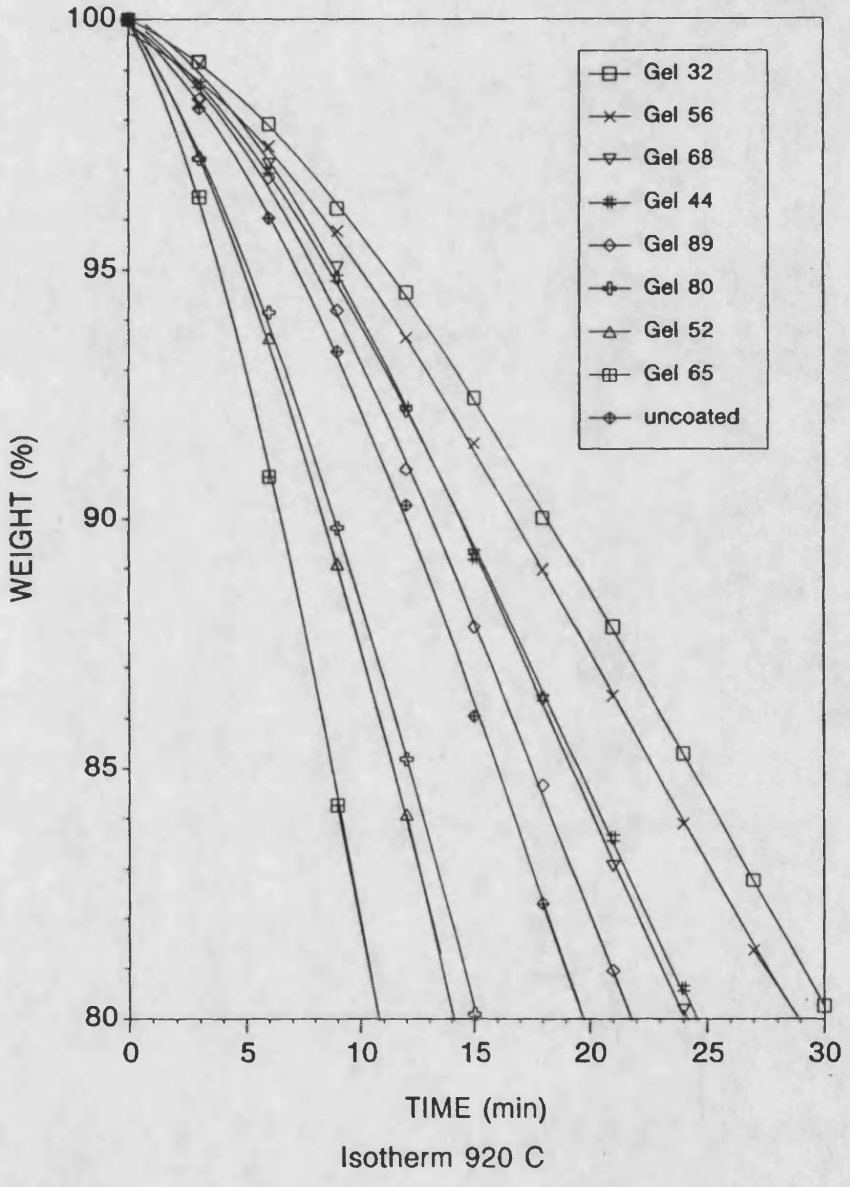


FIGURE 61 - Comparative TGA results for electrode graphite samples fired twice.

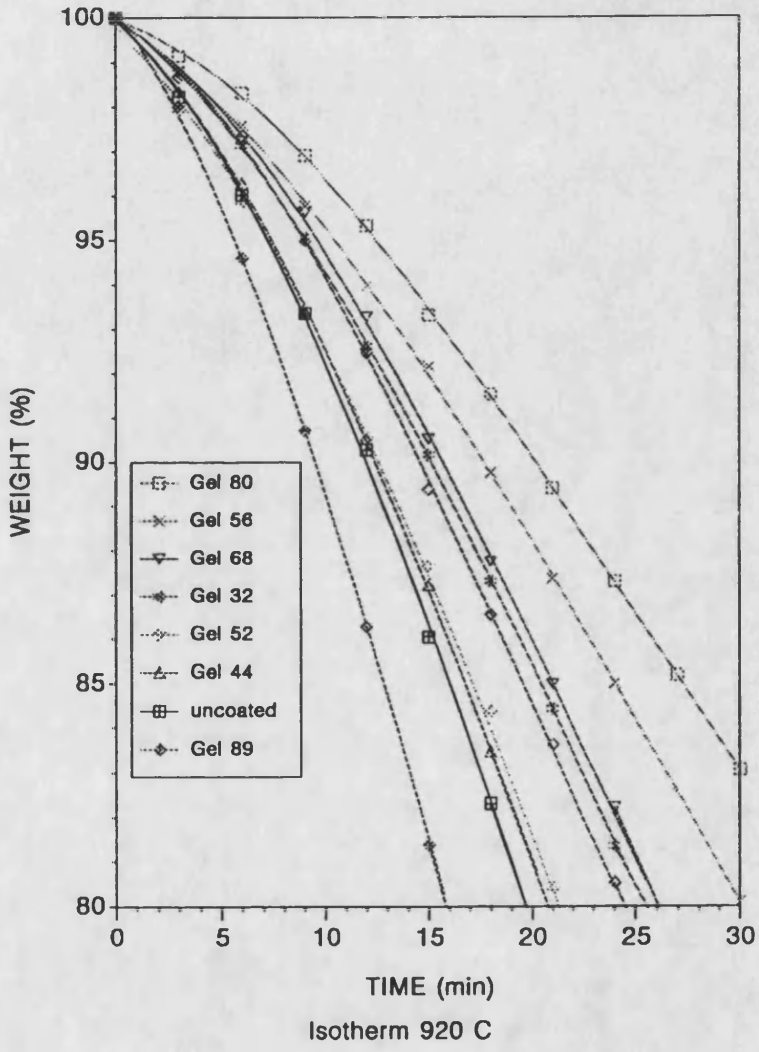


FIGURE 62 - Comparative TGA results for electrode graphite samples fired three times.

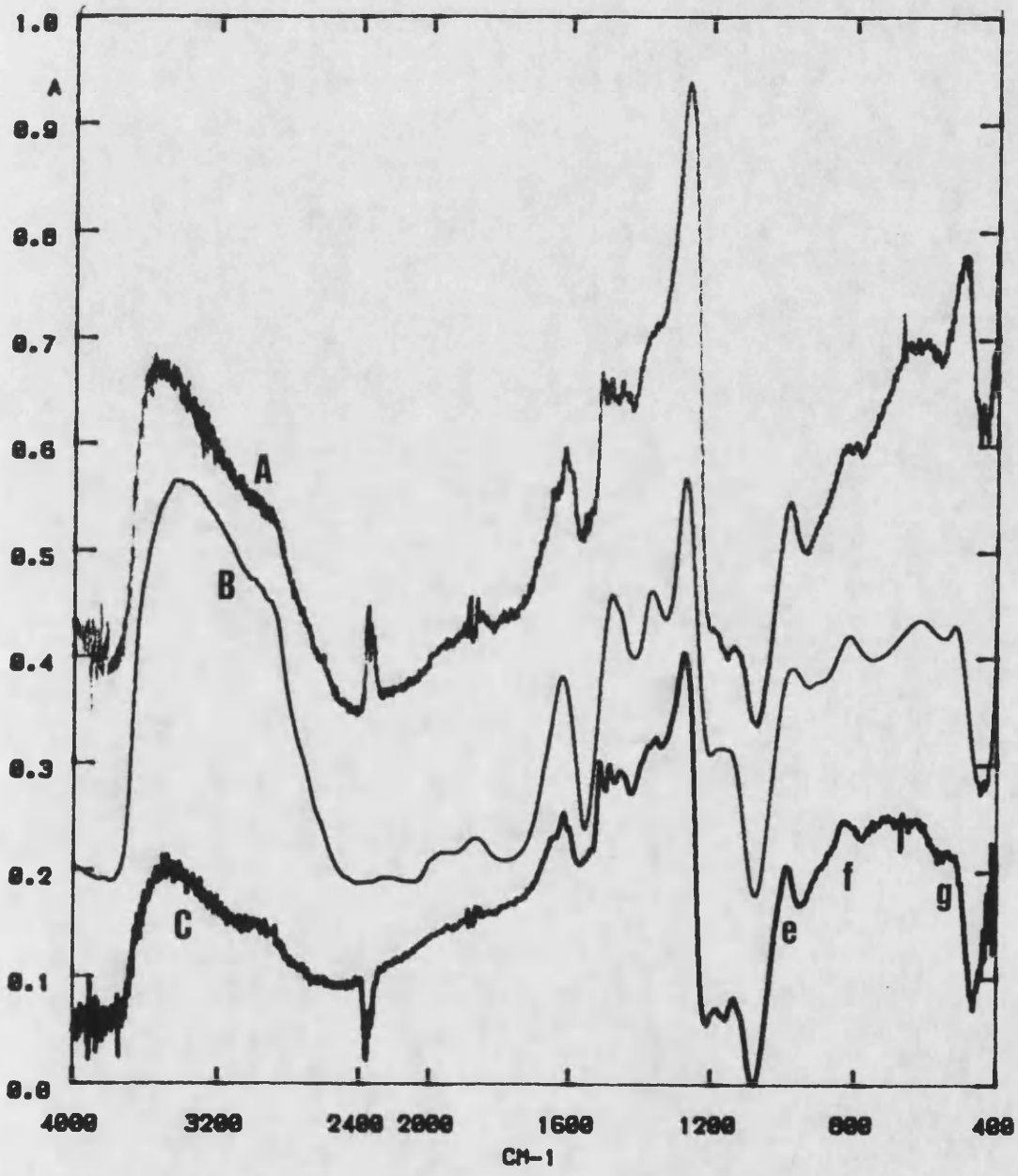


FIGURE 63- FT-IR spectra of the gels 8Ac (A), 56 (B) and 8Eth (C).

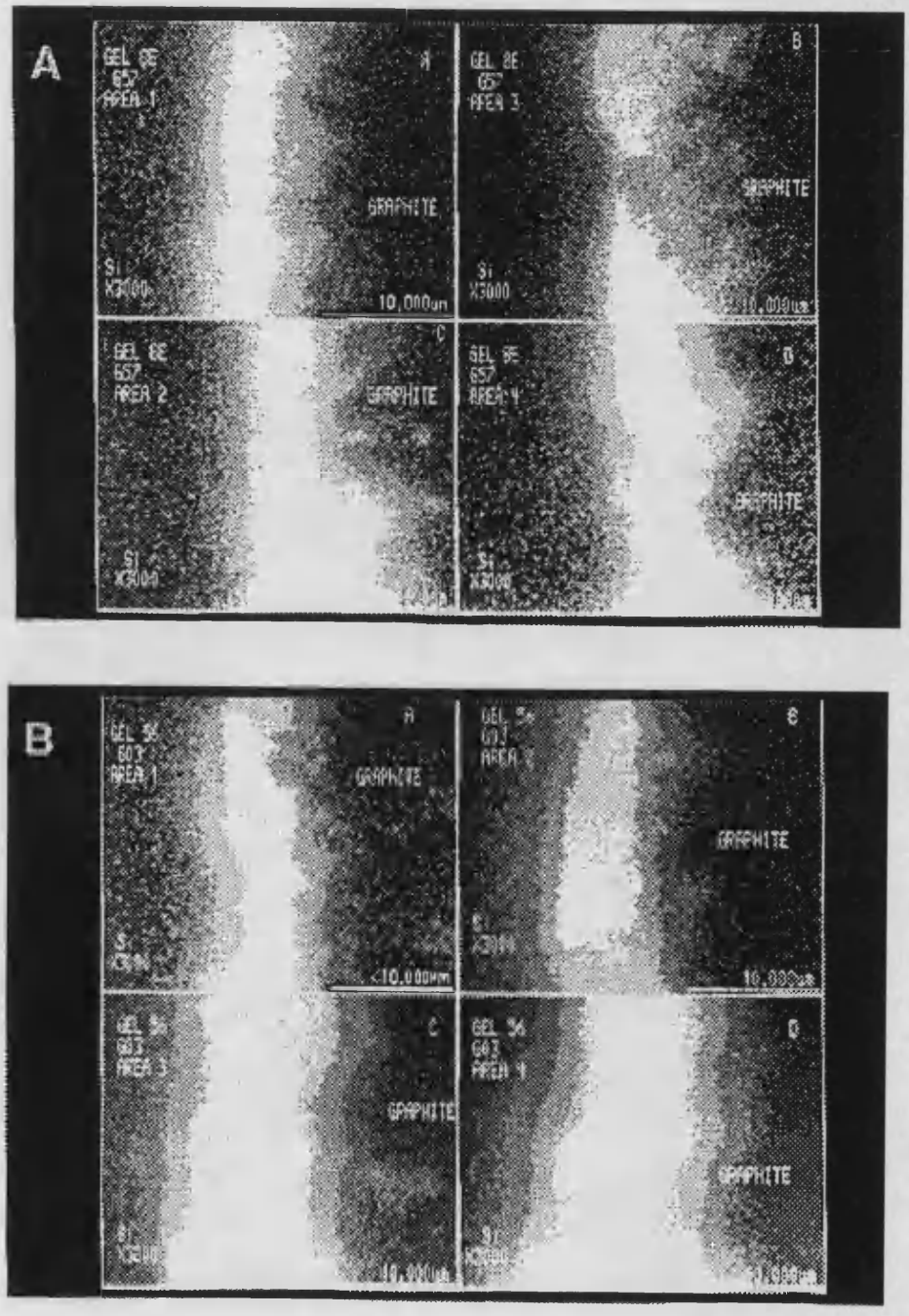


FIGURE 64- EDX image for Si on ZXF 5Q POCO graphite, produced, after five firings, by the gels 8Eth (A) and 56 (B).

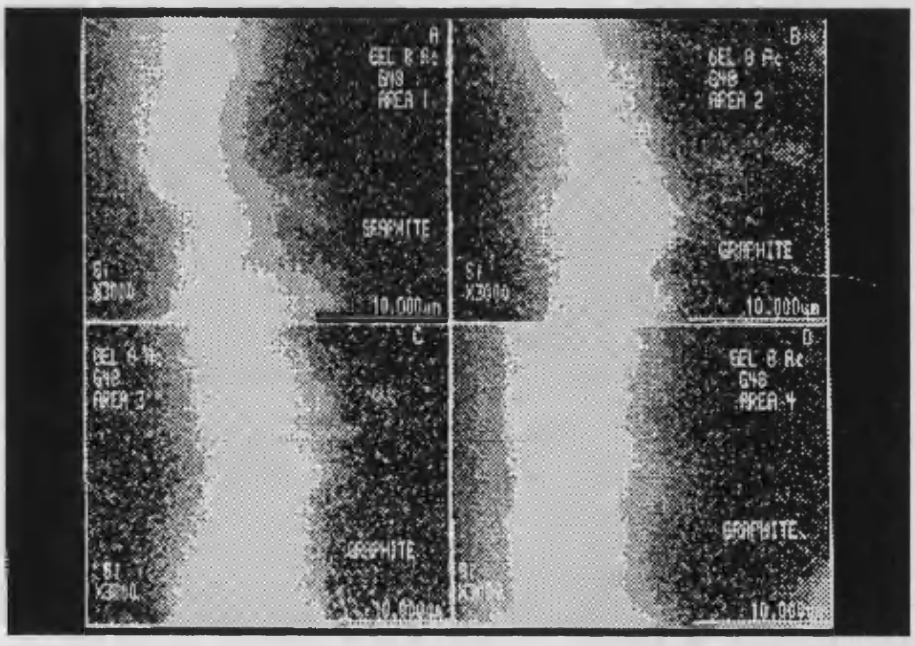


FIGURE 65- EDX image for Si on ZXF 5Q POCO graphite, produced, after five firings, by the gel 8Ac.

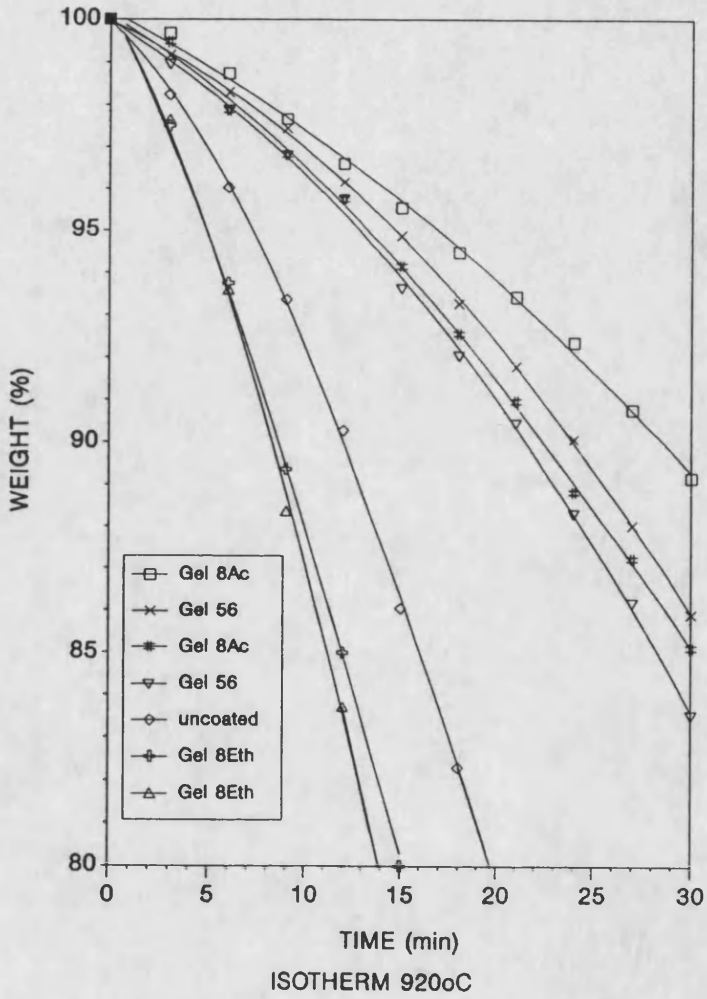


FIGURE 66- Comparative TGA results for the SiC coatings produced from the formulations developed to enhance the gel composition.

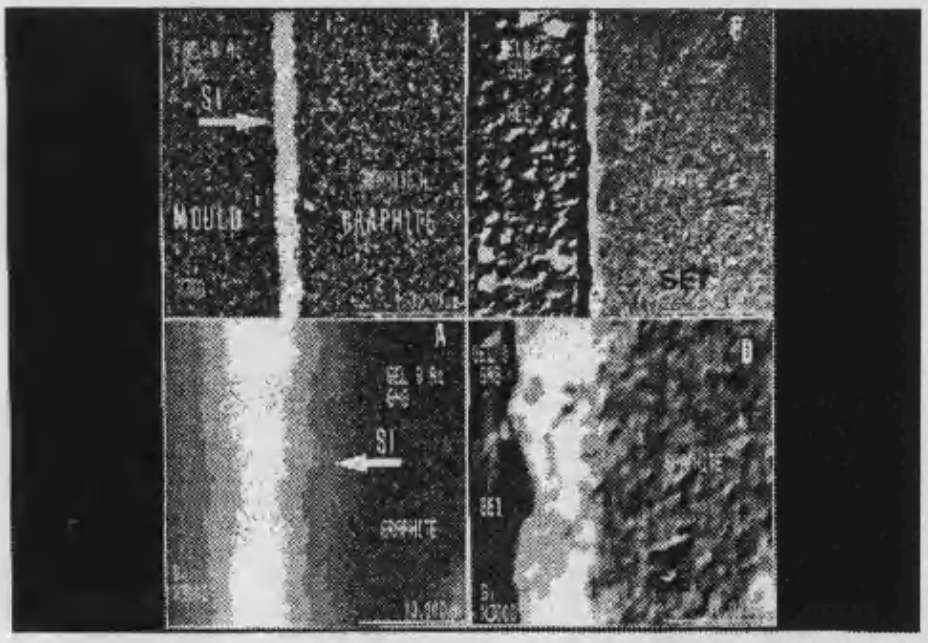


FIGURE 67- A. EDX image for Si on Poco graphite - 300X magnification. B. Secondary Electron Image of Poco graphite.

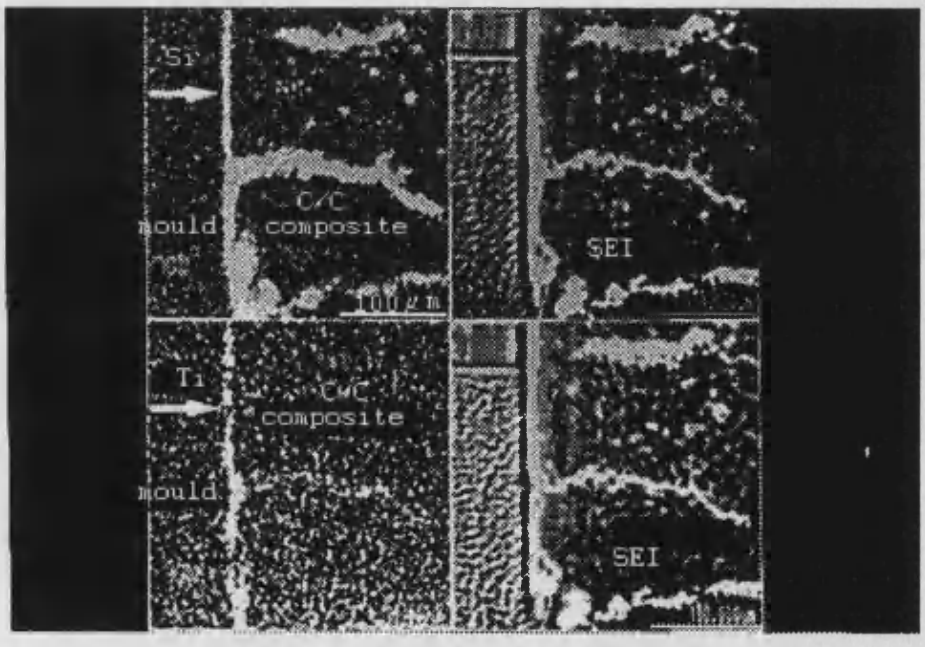


FIGURE 68- A. EDX image for Si and Ti on KKarb C/C composite - 300X magnification. B. Secondary Electron Image of KKarb C/C composite.

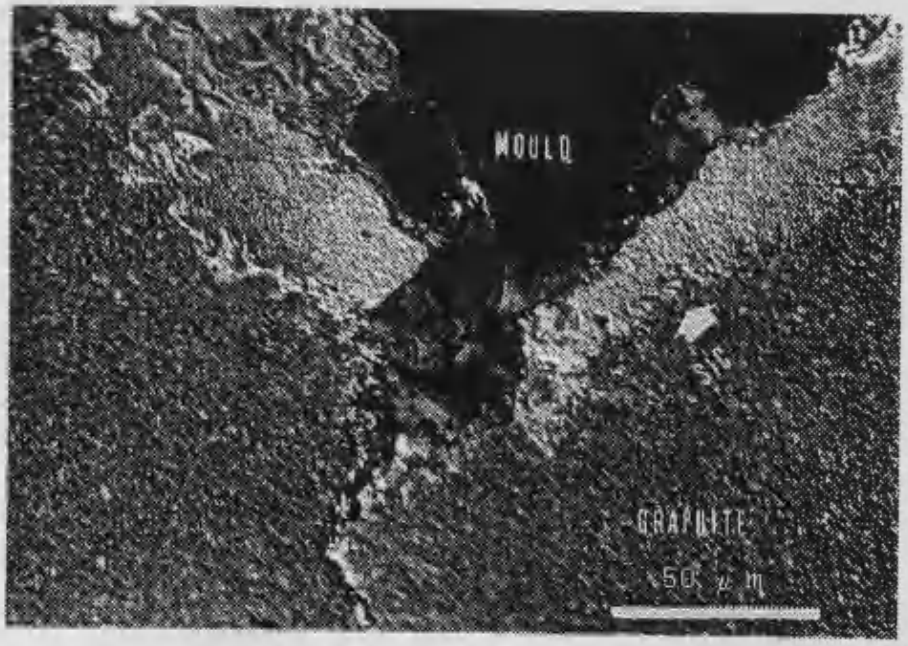


FIGURE 69 Optical micrograph of SiC coating on Poco graphite.

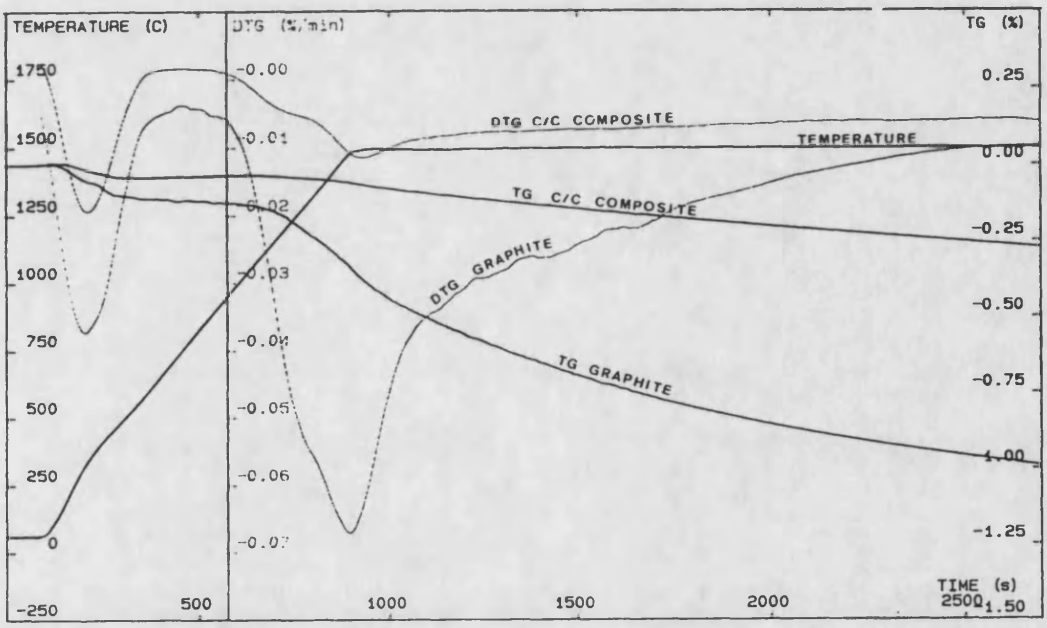


FIGURE 70- TGA of a Poco graphite and a KKarb C/C composite (heat treated at 1500°C during 20 hours in Ar) samples in Helium (flow - 1l/h).

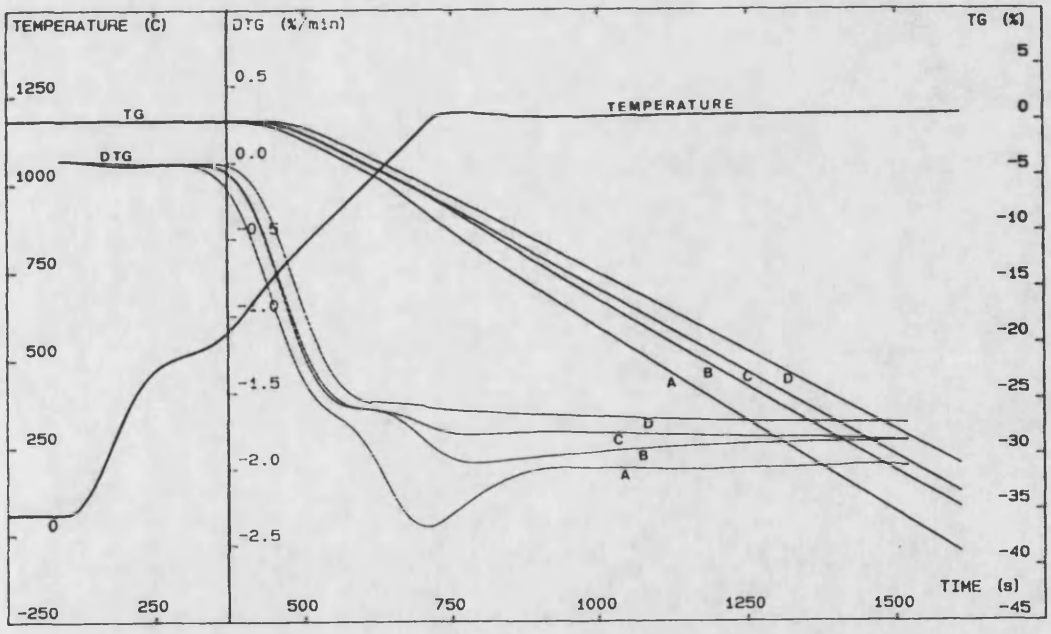


FIGURE 71- TGA for uncoated and coated (with SiC) Poco graphite samples. A. uncoated. B. fired once. C. fired three times. D. fired five times.

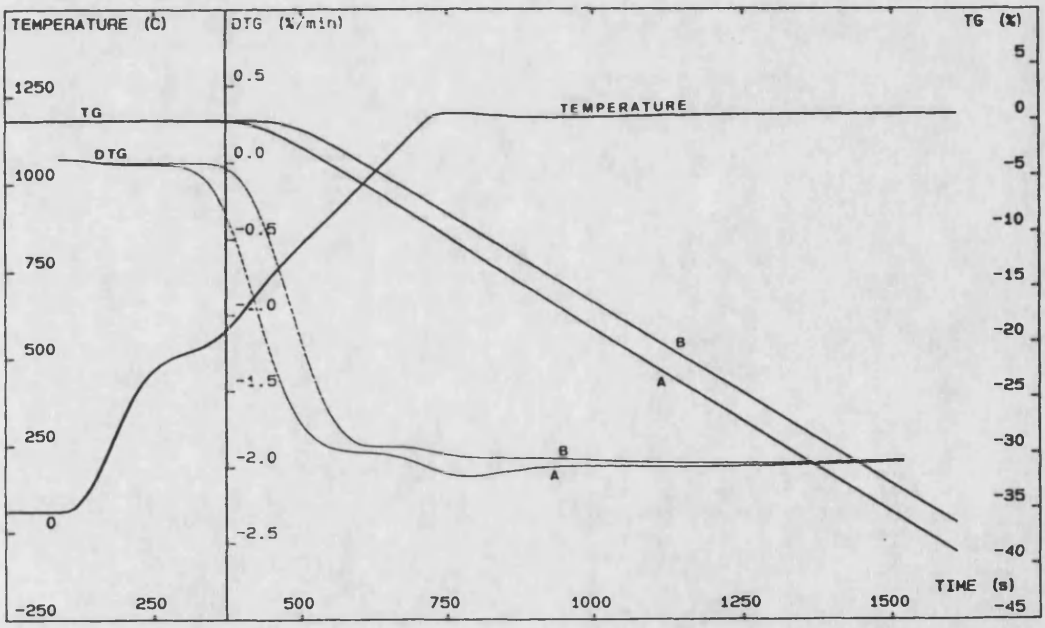


FIGURE 72- TGA for uncoated and coated (with SiC) KKarb C/C composite samples. A. uncoated. B. fired five times.

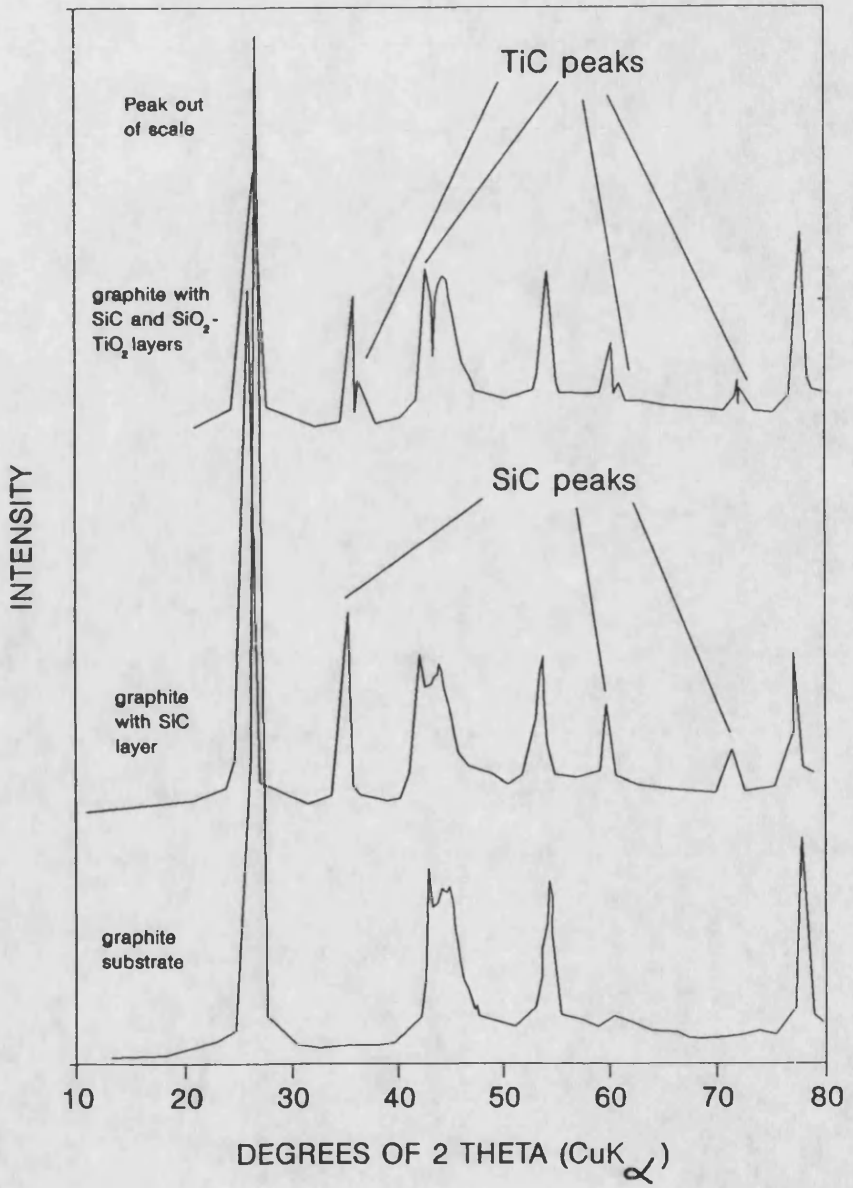


FIGURE 73- X-Ray diffractrogram for a Poco graphite sample coated with SiC and SiO_2-TiO_2 glass fired according the procedure number 1 (section IV.4.1).

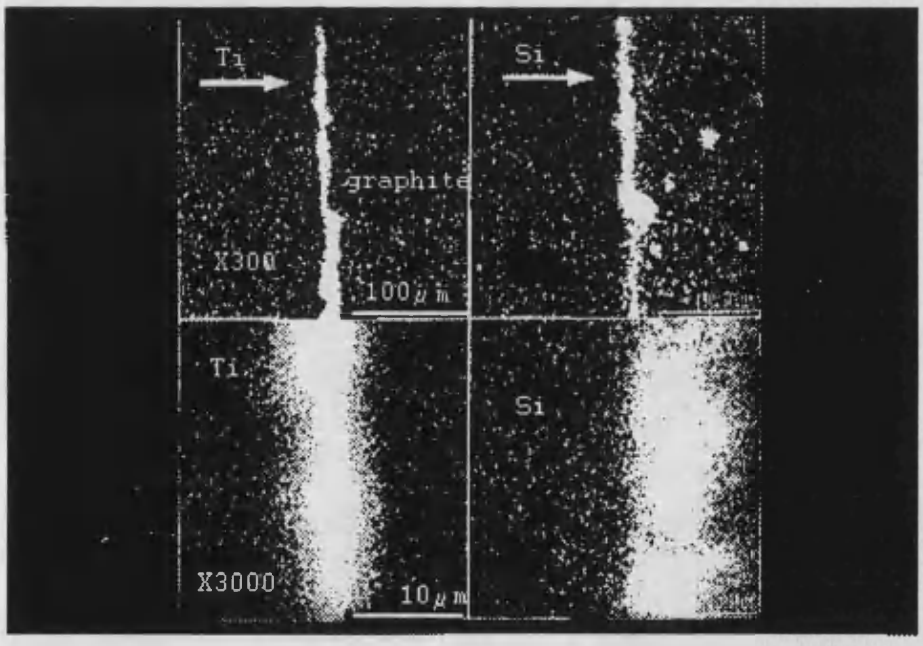


FIGURE 74- EDX image for Si and Ti (before heat treatment up to 1600°C) on Poco graphite.

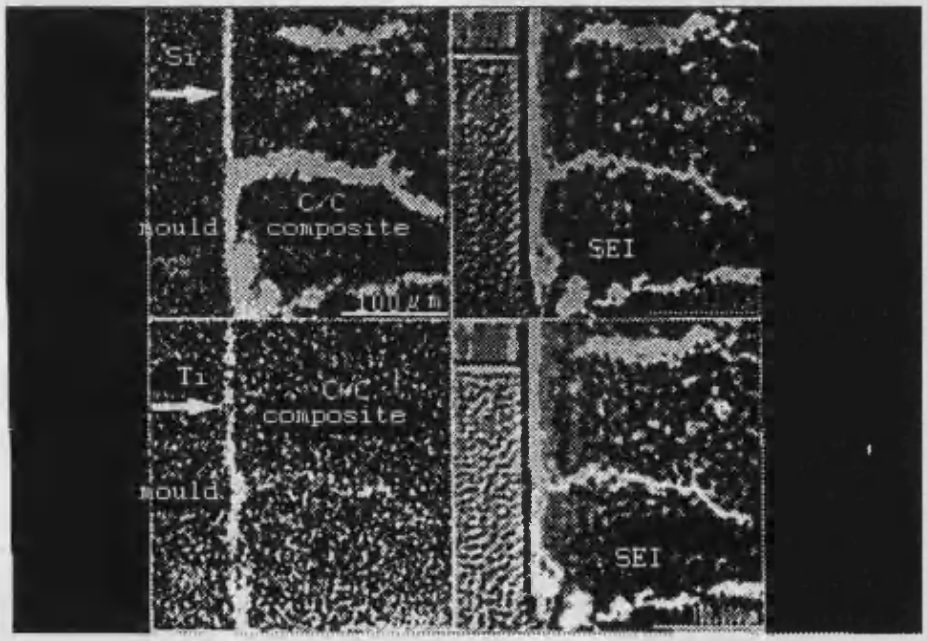


FIGURE 75- EDX image for Si and Ti (before heat treatment up to 1600°C) on KKarb C/C composite.

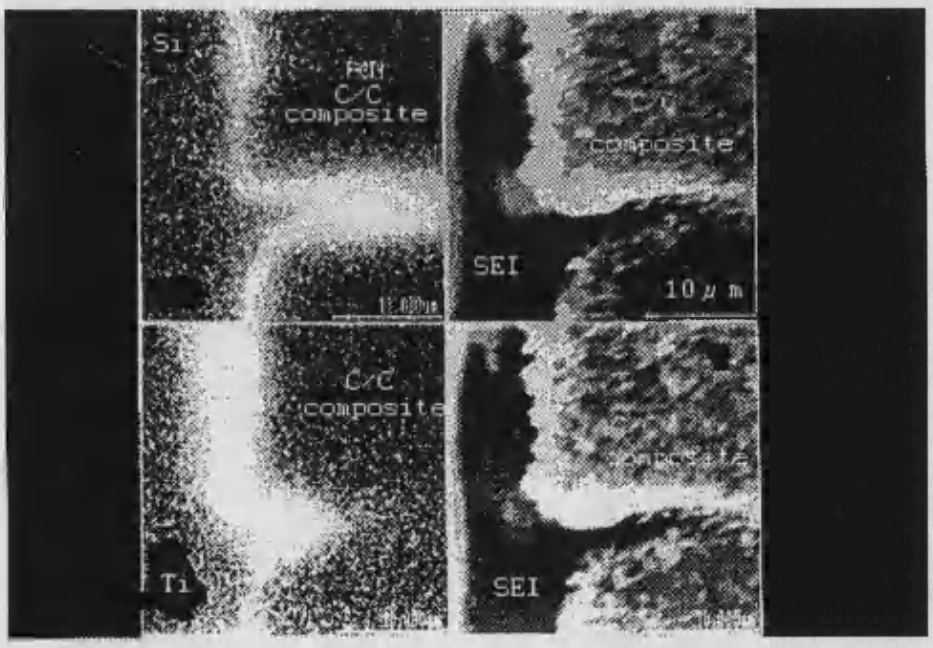


FIGURE 76- EDX image for Si and Ti (before heat treatment up to 1600°C) inside a single C/C composite pore.

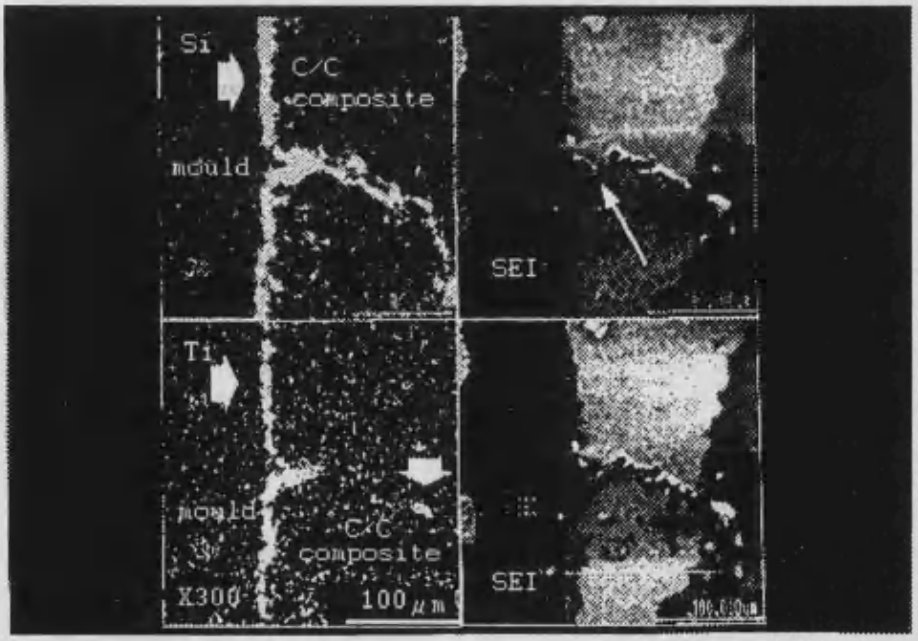


FIGURE 77- EDX image for Si and Ti (after heat treatment up to 1600°C) inside a single C/C composite pore.

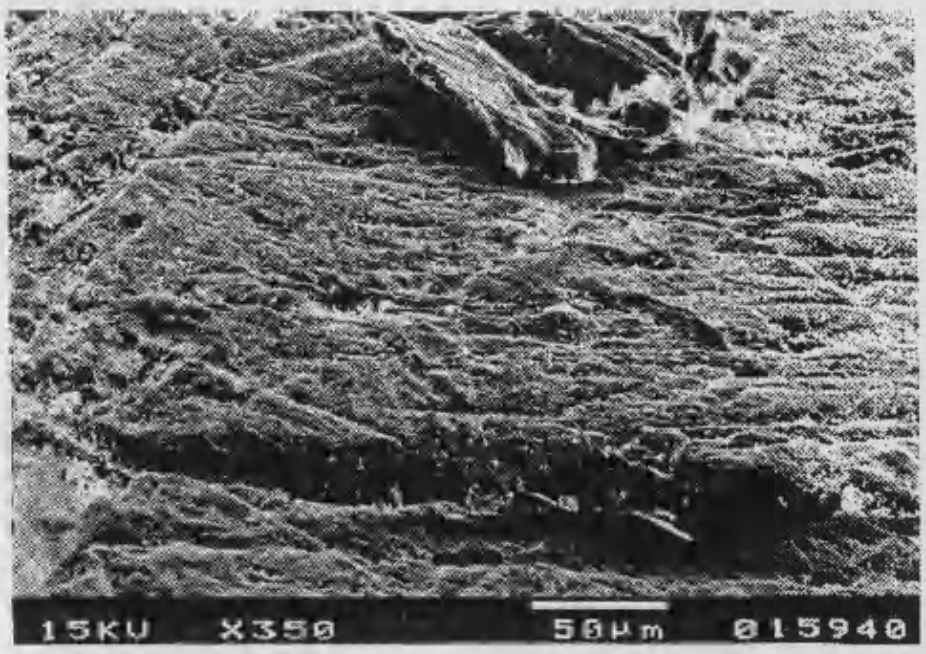


FIGURE 78- Top surface of a C/C composite sample coated with SiC and SiO_2-TiO_2 layers heat treated up to 1600°C), showing the defects of the coating.

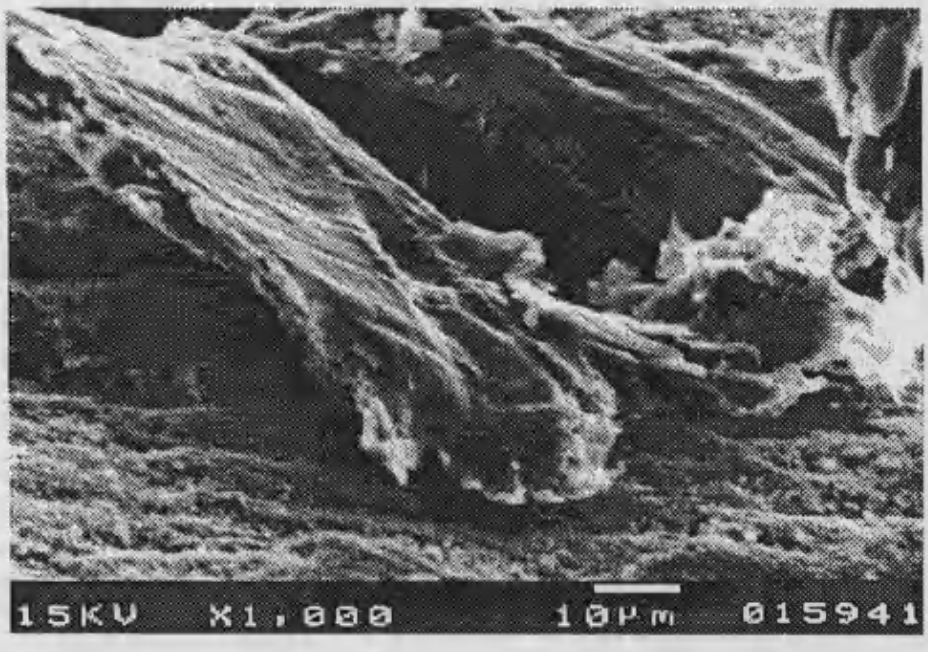
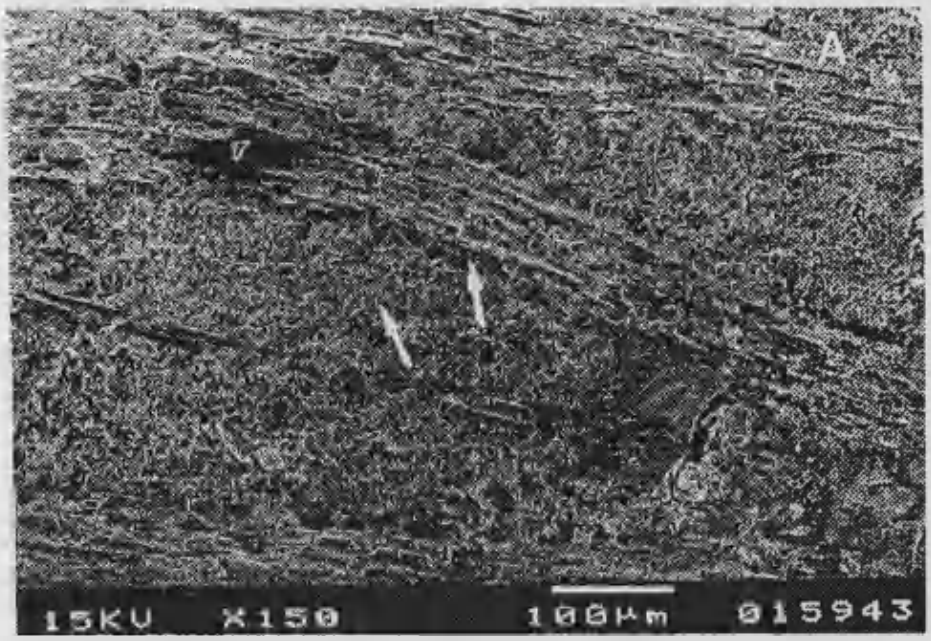


FIGURE 79 Magnification of the defect observed on the top surface of the C/C composite sample coated with SiC and SiO_2-TiO_2 layers heat treated up to 1600°C).



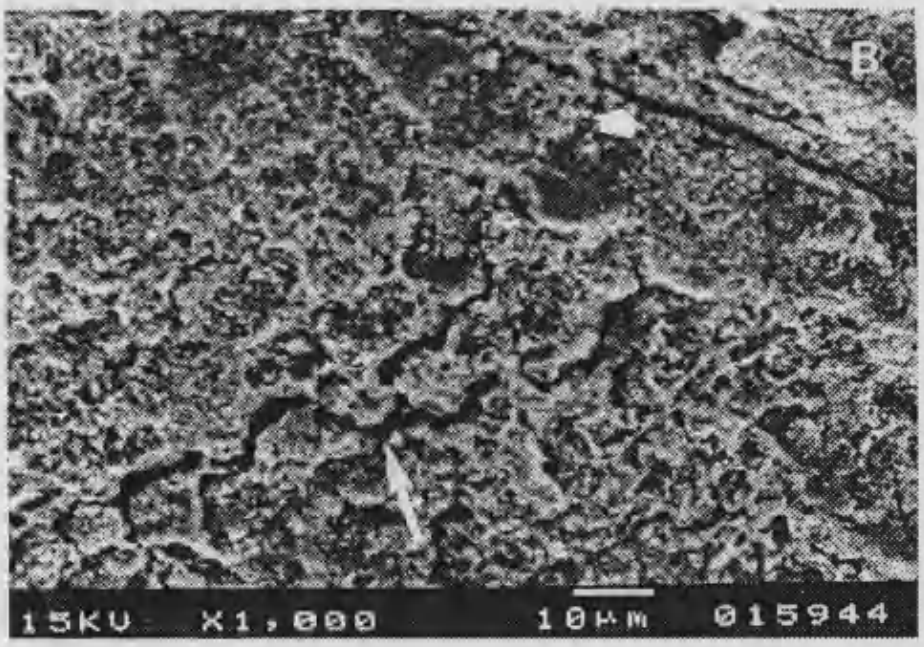
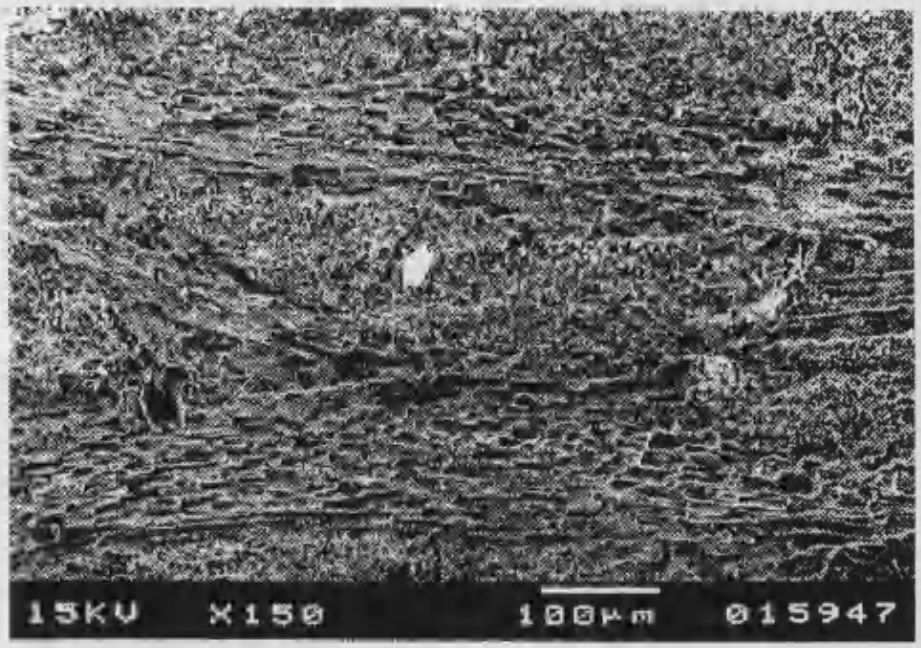


FIGURE 80- A. Lateral surface of a C/C composite sample coated with SiC and SiO_2-TiO_2 layers (heat treated up to 1600°C) showing cracks in the middle of the fibers bundles and along the fibers and the matrix. B. Magnification of the cracks.



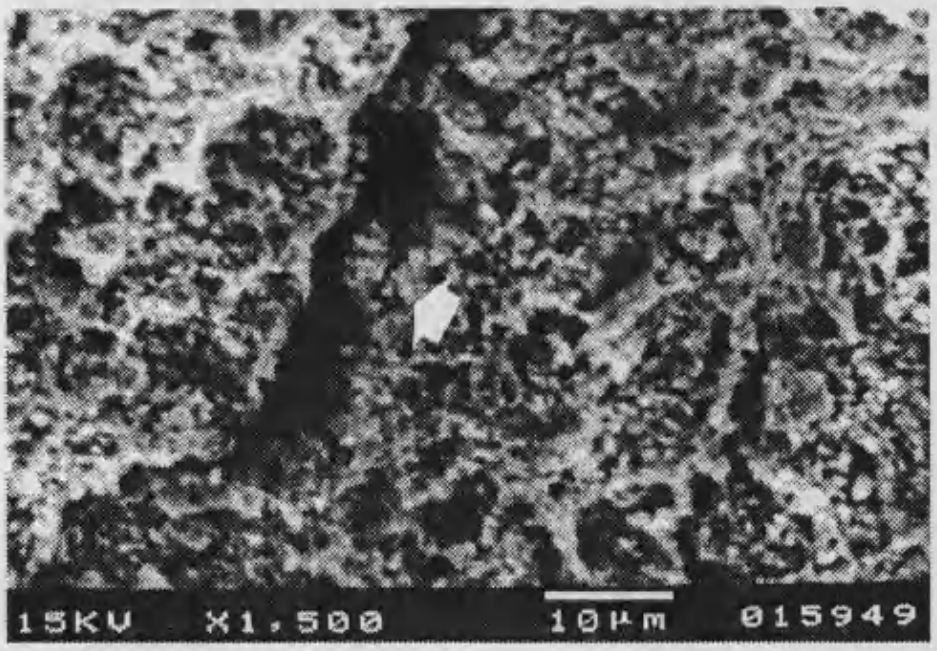


FIGURE 81- A. Lateral surface of a C/C composite sample coated with SiC and SiO_2-TiO_2 layers (heat treated up to 1600°C) showing a crack in the middle of the fibers bundles. B. Magnification of the crack.

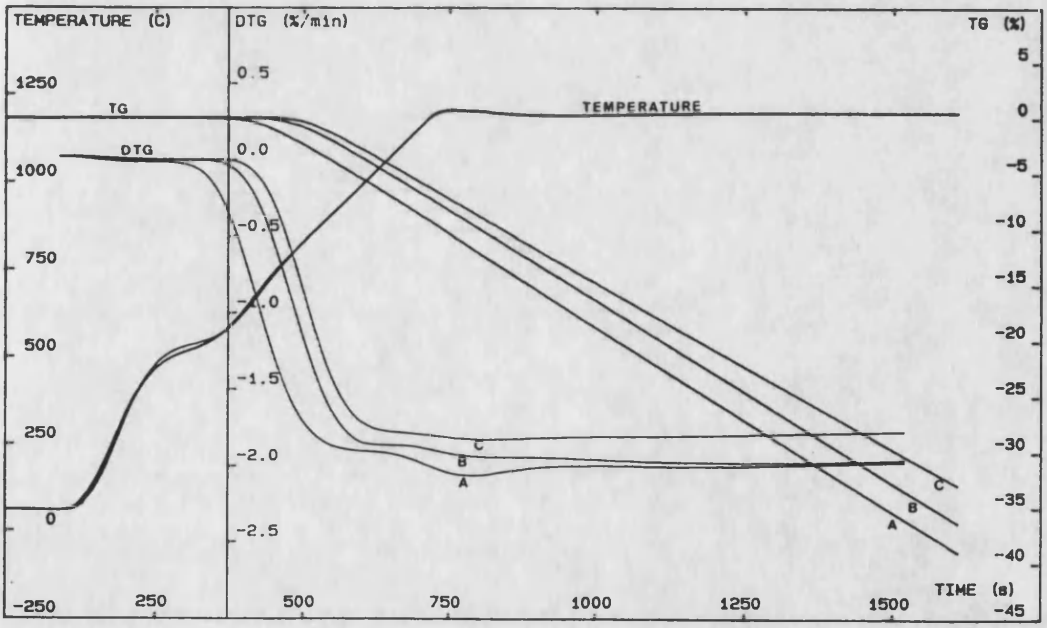


FIGURE 82- TGA of KKarb C/C composite samples. A. uncoated. B. fired five times with SiC. C. fired five times with SiC and four times with SiO_2-TiO_2 glass heat treated up to 1600°C.

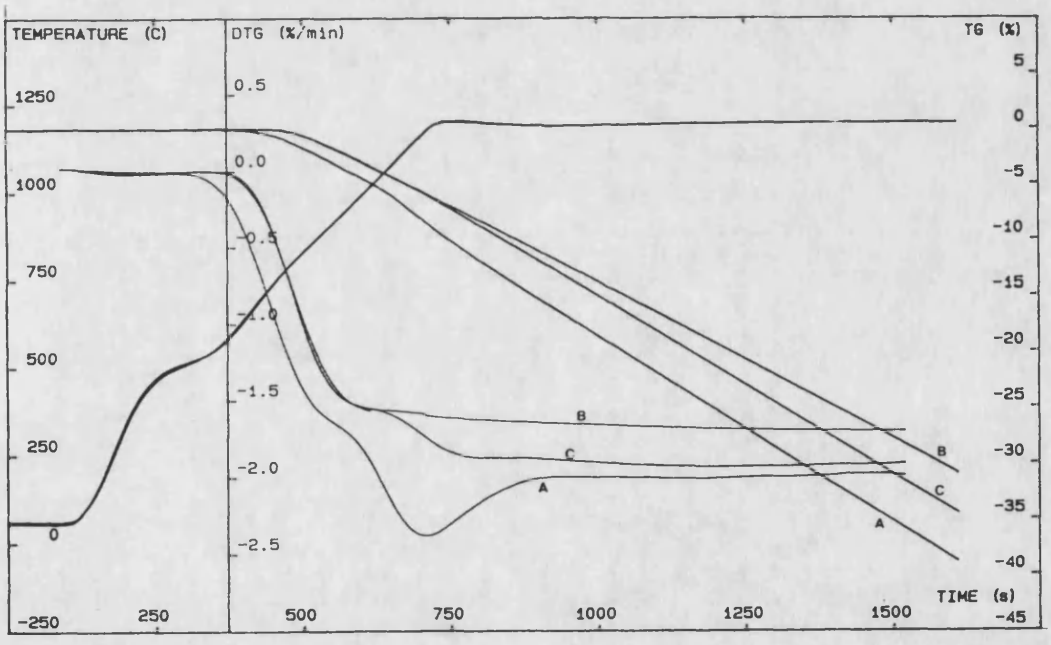


FIGURE 83- TGA of Poco graphite samples. A. uncoated. B. fired five times with SiC. C. fired five times with SiC and four times with SiO_2-TiO_2 glass heat treated up to 1600°C.

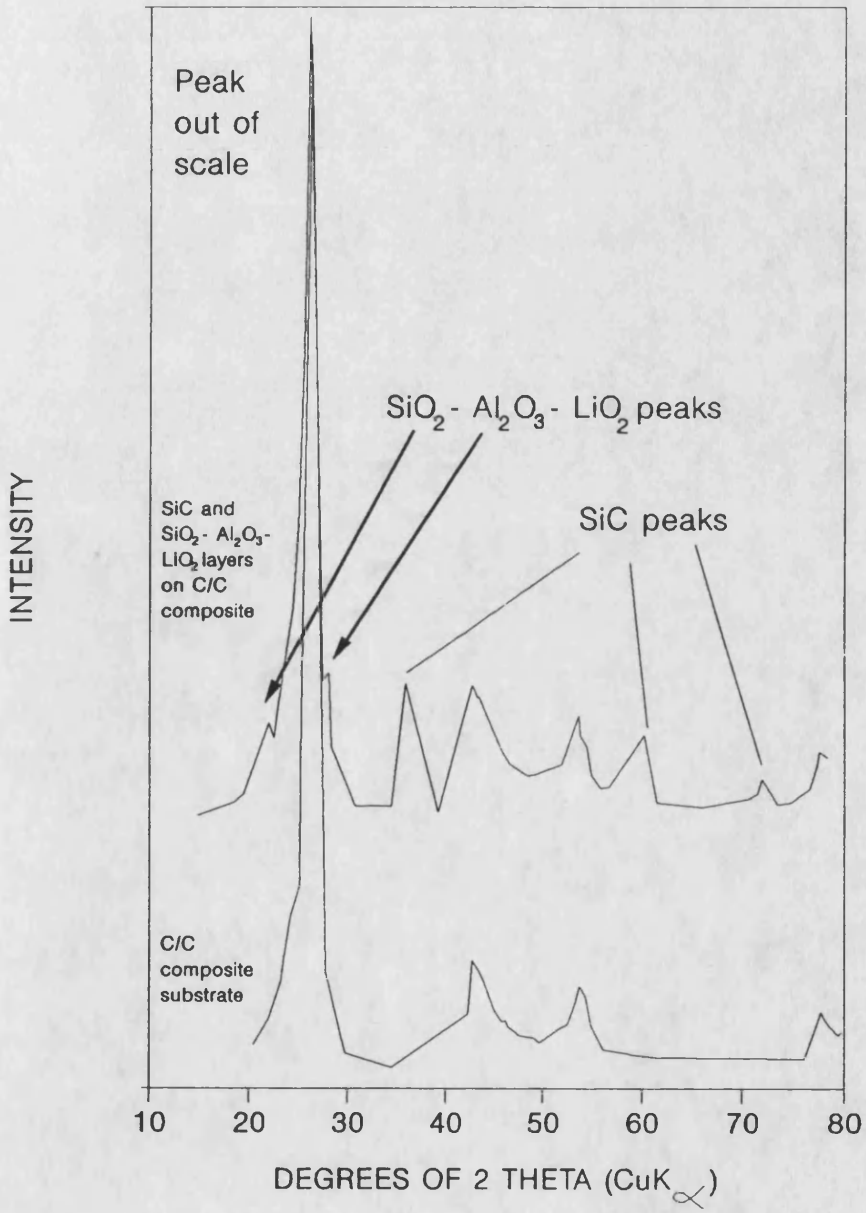


FIGURE 84- X-Ray diffractrogram for a C/C composite sample coated with SiC and with SiO_2-Al_2O_3-LiO_2 glass-ceramic after firing.

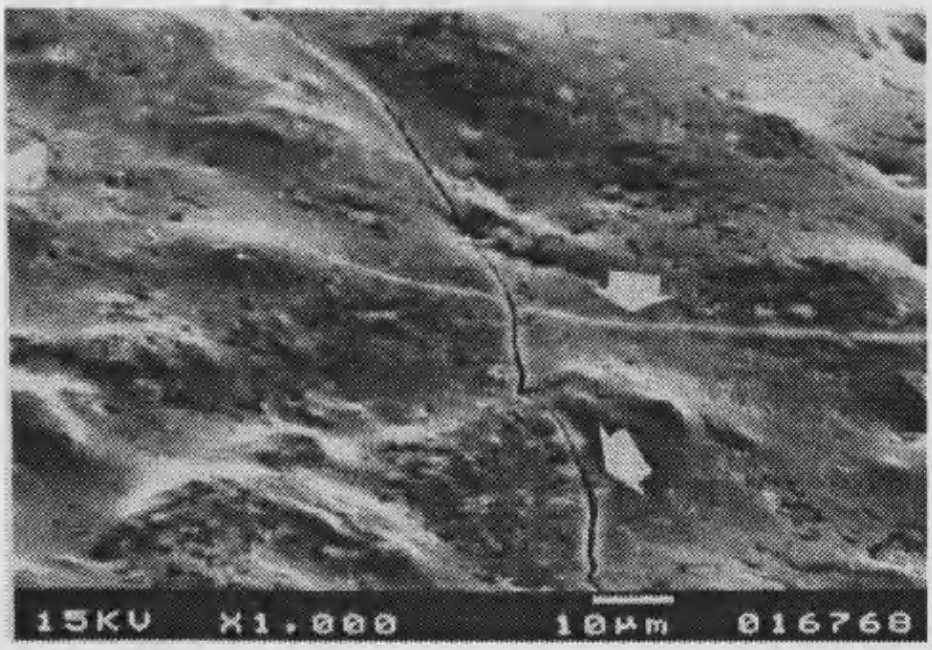


FIGURE 85- C/C composite surface coated with SiO_2-Al_2O_3-LiO_2 glass-ceramic after firing showing the hair-line cracks produced after being sintered.

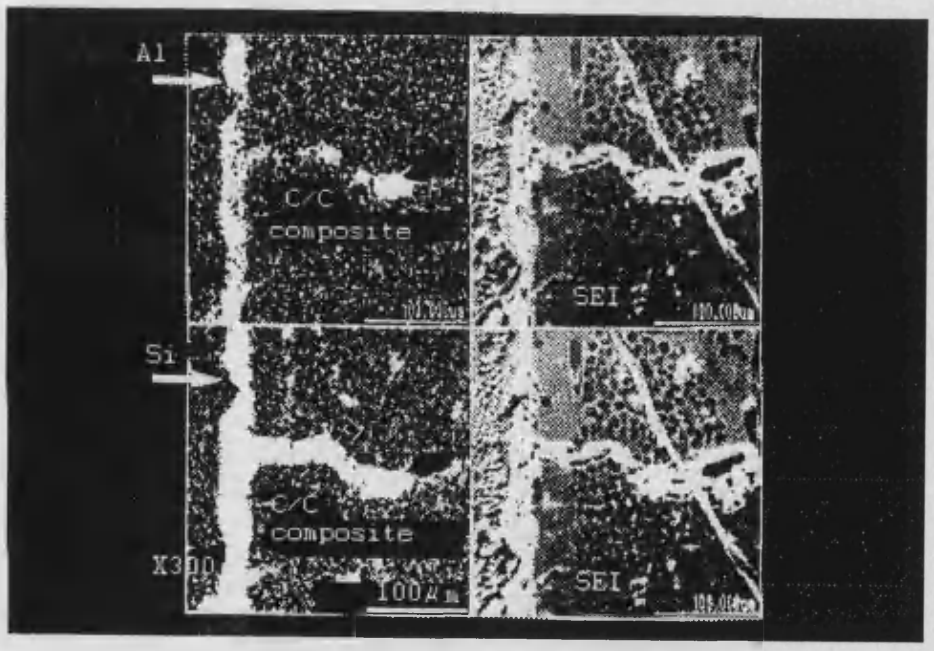


FIGURE 86- EDX image for Al showing the penetration of the SiO_2-Al_2O_3-LiO_2 inside the C/C composite cracks.

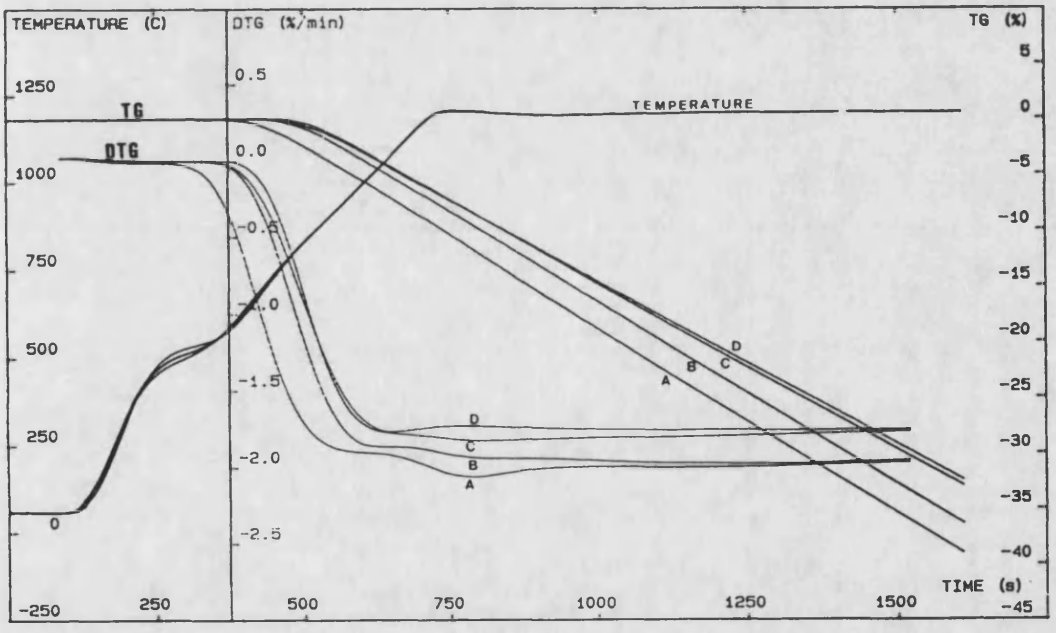


FIGURE 87- TGA of KKarb C/C composite samples. A.uncoated. B.fired five times with SiC. C.fired five times with SiC and four times with SiO_2-TiO_2 glass (heat treated up to 1600°C). D.fired five times with SiC and four times with SiO_2-Al_2O_3-LiO_2.

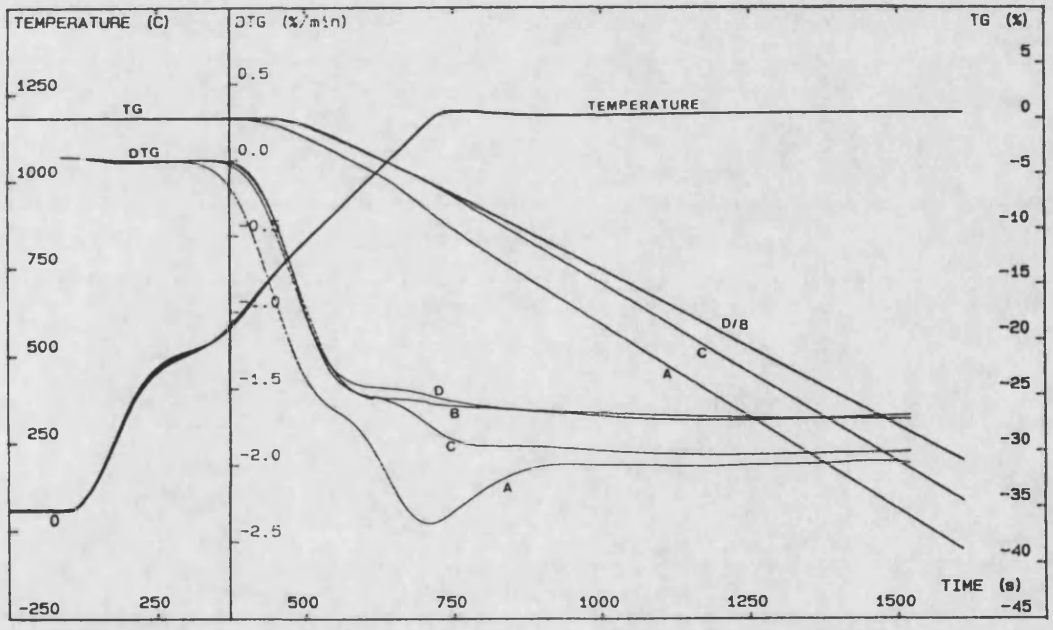


FIGURE 88- TGA of Poco graphite samples. A.uncoated. B.fired five times with SiC. C.fired five times with SiC and four times with SiO_2-TiO_2 glass (heat treated up to 1600°C). D.fired five times with SiC and four times with SiO_2-Al_2O_3-LiO_2.

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